Chem Ed

EDITORIALLY SPEAKING

"Retreading the Chemistry Teacher," Arthur F. Scott's SAMA award address published in this issue, is a keenly penetrating analysis of a crucial problem. Many who heard his remarks at Cleveland began to turn their critical gaze inward at their own careers. As is usually the case when a problem comes into clear focus, corollary problems begin to emerge. One such shattering of complacency can be phrased thus: "Granted that I could ever find myself in that Utopian state of being able to keep up to date, how can I manage to do the same for my students?" The challenge which must be faced is, "Am I making sure that my students are well informed by *today's* standards, not by those I met when my career began?"

Dr. Scott suggests that the *rate* at which chemical knowledge expands doubles every 13 years. Does this mean that a teacher must be covering twice as much material in his course today as he did only 13 years ago? It might well be argued that this is his obligation if he is to graduate a present student at a relative level of competence equal to that he provided for the 13-year alumnus.

Obviously, students being what they are—approximately constant in ability, efficiency, and ambition over a 13-year period—the teacher cannot cover two books instead of one or assign 30 experiments in place of 15. Likewise it is not possible to apply simple arithmetic to the curriculum and double course requirements for the college chemistry major.

The answer to this continuing challenge to the chemistry teacher has to be found in how he teaches his subject. He constantly must be critical of the content of his courses and be willing to modify by replacement rather than merely by accretion as the years go on. It is the honest and courageous professor who rips up the notes of his favorite lecture—or leaves in the file the problem assignment that "really drove the point home." This he must do if old favorites have become engulfed by broader, more significant topics.

There are certain built-in aspects of chemical science which keep the problem from being a dilemma for the chemistry teacher. One invariably emerges from arguments on the proper ratio of descriptive to theoretical course content material. Modern science, in Conant's apt phrase, is constantly "lowering the level of empiricism." Correlating theories exist today that make more meaningful and hence better retained the isolated factual information of yesterday. Even before theories appear, scientific laws emphasizing the relationships between events make possible the efficiency of prediction over trial and error. Teachers who approach the subject from this realization need to go one step farther and be a little obvious sometimes to get a student to recognize this point of view. It can help him to make best use of the years he is investing in his training for a scientific career.

Another efficiency device constantly being used by perceptive teachers is the laboratory experiment that teaches more than one principle rather than merely a single technique. Particularly in introductory courses can one stone kill many birds. For example, a study of the Szilard-Chalmers reaction of manganese will not only introduce the physical chemistry student to radiochemistry techniques but also will provide data for a study of statistical analysis and first order kinetics. Another student time-saver is the use of a whole class, each student establishing one point on a curve. Not only does this save time, but also it emphasizes how often today's practising scientist must operate as one of a group.

Just as Dr. Scott sees ways to solve, at least partially, the problem of keeping the chemistry teacher up to date, there are ways of accomplishing more and better student training in less time. Along with keeping up to date, this is one of the most demanding challenges to the ingenuity of the teacher. His meeting that challenge may be the very thing which will make him do what he hopes his students are learning to do: to use their minds creatively to solve problems. Students will be poor chemists later if in school all they have to do is sort through an encyclopedic mental card file until the answer to an identical previous question falls out. Teachers *are* poor chemists if, similarly, preparation for a lecture means reliance on the filing cabinet instead of the imagination.

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Retreading the Chemistry Teacher

During the past few years chemists have come to use the word "retreading" to characterize a situation or problem that has arisen in the teaching of chemistry in high schools and undergraduate colleges. The term is supposed to suggest that a teacher's academic casing is thin not because of wear but by comparison with the latest models. It is implied further that the teacher is able and well trained and has not kept up-to-date only because circumstances did not permit it. To be specific, the problem covered by the term "retreading" is the fact that many of our chemistry teachers must be helped if they are to continue as effective teachers. It is this predicament of chemistry teachers which I wish to discuss tonight.

My definition of "retreading" excludes two groups of teachers: those university teachers, active in research, who contribute to our fountain of chemical knowledge; and the poorly prepared teachers, no matter where they teach. I exclude the university teacher because his research activity obliges him to keep abreast of developments in at least one area of chemistry, which most likely includes the specialized courses he teaches. And I exclude from my definition the poorly prepared teacher who should not be teaching at all. I agree with Polykarp Kusch's proposal[1] that the only sound way of helping teachers who are incompetent because of inadequate training is to undertake a program of subsidies which would enable them to acquire the necessary basic knowledge and experience without cost to themselves.

In my remarks I shall concern myself with a third group—the high school and college chemistry teachers who are well prepared at the start of their careers but whose teaching responsibilities make it difficult for them to keep up with the fast moving chemical world.

Existing Programs

Many organizations have recognized the importance of helping the chemistry teacher and have instituted various types of programs to help them. I will mention one or two of these programs to illustrate both the broad base of their support and the variety in the types of assistance which have been rendered. One of the first organizations to help the high school teacher was the Manufacturing Chemists' Association which is now in the fourth year of its program of developing aid-to-education material[2] such as improved laboratory experiments. In another effort to help chemical education the Crown-Zellerbach Foundation provided funds three years ago to bring together a group of high school and college teachers to discuss the whole problem of chemistry instruction in high schools;[3] and as a result of this conference the NSF is now supporting both the preparation of a new textbook for high school students and the training of teachers to use this book. Without doubt, the organization which has been and is doing most in the way of retreading the chemistry teacher is the National Science Foundation. The Foundation supported summer institutes as long ago as 1953 and now sponsors a large number of institutes and conferences[4] designed to help the chemistry teacher. There can be no question concerning the value of these various programs of assistance. That we have them in operation today must be credited in large part to the recent officials and committees of our Division of Chemical Education who have been very alert to the problems of chemistry teachers.

Magnitude of the Problem

In order to know the full magnitude of the retreading problem and to evaluate the existing programs designed to solve it one should have information on several points such as: (1) the total number of high school and college chemistry teachers in this country; (2) the fraction of teachers, both in high school and college, whose basic training is adequate; (3) the age distribution of teachers in the "adequate" group; and (4) the percentage of the competent teachers who have taken advantage of the various refresher programs available to them. I doubt that all of this information is available at the present time; at least I have not been able to get my hands on it. About all I can do is to present some information regarding the number of chemistry teachers in this country and to make some guesses on the other points. A recent survey indicates that the number of high school chemistry teachers is very close to 20,000 with slightly more than half of this group also teaching physics. I cannot offer a definite figure for college teachers. There are, however, 861 institutions offering a bachelor's degree in physical sciences with only one-

The 1960 Scientific Apparatus Maker's Award in Chemical Education address given before the dinner meeting of the Division of Chemical Education at the 137th Meeting of the American Chemical Society, Cleveland, April 11, 1960.

[1] See Polykarp Kusch's paper "Education for Scientific Literacy in Physics," presented at the Tenth Thomas Alva Edison Foundation Institute "Reconstructing Scientific Education for All," November 19–20, 1959.

[2] A description of this material is to be found in the recent pamphlet "An Industry Aids Our Schools," a 1960 report of the program of the chemical industry.

[3] "The Reed College Conference on the Teaching of Chemistry," J. CHEM. EDUC., **35**, 54 (1958); and STRONG, L. E., AND WILSON, M. K., "Chemical Bonds: A Central Theme for High School Chemistry," J. CHEM. EDUC., **35**, 56 (1958).

[4] A summary of these activities is to be found in the pamphlet "NSF Programs for Education in the Sciences," March, 1959.

fourth of them offering a higher degree. It would seem reasonable, therefore, to suppose that there are 3 to 4000 teachers of undergraduate chemistry. Regarding the age distribution of chemistry teachers we can only surmise that a great many of them in both high school and college groups are under 45 years of age and still have more that 20 years of teaching ahead of them. Although it would be of interest to know the number of teachers who have benefited by the various assistance programs, I doubt that this could be determined now except by means of a nationwide questionnaire. I would guess, however, that the figure would not exceed 20%, both for high school and college teachers.

Programs to help the chemistry teachers of the country are quite recent developments and originated from the realization that the materials which were being presented to high school and college students were both out of date and inadequate. This state of affairs was (and is) generally explained as having come about "because science and technology have developed so rapidly during the past 50 years."[5] Although there can be complete agreement on this very general statement, there still remain unanswered several important questions relating to the future of chemistry teaching. For instance: did the teaching become out of date because the sum total of chemical knowledge had become so great or did the rate of development of new concepts and facts become greater than the busy teacher could handle in the time available to him? Further, are the present programs intended to be only a shot-in-the-arm with the expectation that they will cure the difficulty or are these programs the first steps in a long range treatment which must be continued indefinitely? I certainly am not prepared to attempt answers to these questions. It seems to me, however, that some insight into the problem—present and future—of helping teachers keep up to date can be gained by a better picture of what we mean by the general phrase "science and technology have developed so rapidly." It is this question of the growth of chemical knowledge that I wish to consider particularly here.

Growth of Chemical Knowledge

For our basic picture of the growth of science as a whole we are indebted to Derek Price[6] who has studied the growth of various scientific and technological activities which can be regarded as indices of the general development of science. According to Price, science as a whole has expanded exponentially from about the year 1700 on, the doubling time being about 11 years. For example, Price found that the growth in the total number of scientific journals published has been remarkably exponential for a remarkably long time. Price also deals with the question of when this exponential growth might begin to taper off and expresses the view that in about 25 years a slowing down in the expansion of scientific activity might begin to take place. Of interest also to the special problem of chemistry teachers is Price's estimate that in nonscientific fields the total body of knowledge doubles about every 30–50 years, that is to say, at a very much slower rate than is the case with scientific knowledge.

That Price's conclusions are generally valid for chemical knowledge specifically is supported by Strong and Benfey's recent article[7] in which they show that for the past 50 years the number of scientific indexes in *Chemical Abstracts* has quite clearly increased exponentially, the doubling time being 13 years.

For the purpose of our present discussion we would appear, therefore, to be on fairly safe ground in assuming that chemical knowledge has followed and is following the law of exponential growth with a doubling time of 13 years (corresponding to an annual rate of increase of 5.33%). For the sake of argument, we shall assume further that this law of exponential growth is valid for the period starting with 1860 and ending with the year 2000. The year 1860 is picked arbitrarily as the beginning of chemistry teaching in this country[8] and the year 2000 is chosen as the probable terminal date of the careers of the youngest generation of teachers, that is to say, those who start teaching in 1960.

One consequence of the law of exponential growth is that the *rate* at which chemical knowledge expands also increases exponentially, with the same doubling rate of 13 years.

The Teacher's Own Problem

This law of exponential growth points to several interesting deductions. One of these can be expressed best in terms of the individual teacher's experience. If a teacher's career covers a period of 40 years—that is to say, three doubling periods—then during his career the storehouse of chemical knowledge increases eight-fold, and similarly, the *rate* at which the storehouse expands also increases by a factor of eight.

Although this rule of an eight-fold increase can probably be viewed as generally valid, it does not give a measure of the difference in pressures upon teachers from

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[5] NSF pamphlet referred to above.

[6] Price, Derek J., "The Exponential Curve of Science," *Discovery* (June, 1956).

[7] Strong, L. E., and Benfey, O. T., J. Chem. Educ., **37**, 28 (1960).

[8] The teaching of chemistry in this country got off to a very uneven start. Several of the older eastern universities had someone on the faculty with the title "Professor of Chemistry" before 1800, but formal or regular courses for undergraduates did not make their appearance until after 1850. For example, Charles W. Eliot has recorded that when he entered Harvard College in 1847 no chemistry course was available to undergraduate students, but 10 years later he was assisting Professor Cooke in a laboratory course in mineralogical chemistry. Another dating record is the experience of Ira Remsen who went to Williams College in 1872 as professor of physics and chemistry and found that no laboratory existed. By the end of the year, however, he had persuaded the trustees to provide a small laboratory for his own use; one for class instruction came along a year or two later. The spirit of the times with respect to the teaching of chemistry is revealed by the advice Remsen received from the college president his first year at Williams: "The students who come here are not to be trained as chemists . . . They are to be taught the great fundamental truths of all sciences. The object aimed at is culture, not practical knowledge." The teaching of chemistry in high schools certainly followed that in colleges by 10 years or more. From the foregoing it would appear that 1860 is about the earliest date we could choose as the starting date for the teaching of chemistry. In other words the formal teaching of chemistry is barely 100 years old. For an interesting discussion of the early history of chemistry see Lyman C. Newell's article "The Founders of Chemistry in America" in the J. Chem. Educ., **1**, 48 (1924).

one generation to another. To get an approximate picture of the variation in these pressures at different periods in the history of chemical education I have carried out the following calculation. First, I have assigned a value of unity to the total of chemical knowledge in the year 1860 and for the sake of simplicity will refer hereafter to this unit of chemical knowledge as a "khem." Then, by means of the exponential function which gives a doubling period of 13 years, I have calculated for seven different years of especial interest to us as chemistry teachers, both "khem" values and the "khem per year" values. The results of these calculations are as follows:

Year	Event	Sum of chemical knowledge in "khem" units	Rate of expansion of chemical knowledge "khem"/year
1860	Assumed start of teaching of chemistry	1	0.05
1876	Founding of American Chemical Society	2	0.1
1907	Start of *Chemical Abstracts*	12	0.6
1923	Organization of Division of Chemical Education	29	1.5
1946	Start of post-war period	99	5
1960	Present	206	11
2000	Probable termination date of teacher whose career started in 1960	1750	92

A number of interesting speculations can be based on the calculated "khem" values. One point can be stated in terms of the experience of teachers of my own age, those of us who started teaching in 1923, the same year that the Division of Chemical Education was launched. During the 37 year period 1923 to 1960 the khem scale increased from 29 to 206 or 177 units. The young chemistry teacher who starts his career in 1960 will experience this same increase of 177 "khems" by about 1972, or 12 years from now.

It is an interesting exercise to try to ascertain the approximate point at which teachers first began to experience difficulty in keeping up with developments and incorporating them into their regular courses. One thing is certain: when the Division of Chemical Education was organized in 1923 the teachers of chemistry had no sense of pressure on them. How else could we account for Neil Gordon's editorial comment in the fifth issue of the first volume of the JOURNAL OF CHEMICAL EDUCATION?

> This has not been true in the past. Many men and women and especially the former have gone into the teaching of chemistry with the feeling that they would teach for a while and then shift into the industries. As a rule, the drift is now in the opposite direction.

It seems reasonable to assume, however, that teachers and others became seriously concerned about the problem of keeping chemistry courses up to date sometime after the war—say in the late 40's or early 50's—when according to our scale the accumulated chemical knowledge would be about 150 khems. The exact numerical value is, of course, of no importance. The point, however, should be fairly clear: if chemistry continues to develop and expand as it has in the past, the teacher who starts his teaching career this fall will end it 40 years from now in a chemical world in which the sum total of chemical knowledge and the *rate* of expansion of this knowledge is of the order of 10 times greater than that which first created serious difficulties for the present generation of chemistry teachers. The prospect can be pictured in still another way. In the year 2000 the annual rate of expansion of chemical knowledge would approximate the total body of chemical knowledge at the end of World War II.

Of course, it is quite possible that the growth of chemical knowledge will not continue exponentially. Yet, even if our forecasts should be off by a factor of two, the situation would be serious enough. My purpose in going through the foregoing calculations is to indicate that the retreading problem is hardly temporary but is almost certainly a continuing one. It is my contention that we would be well-advised to develop some long range plans to deal with it.

If my speculations are on the right track, they indicate that we are moving into an era without precedent in the history of chemical education, one in which there must be provided, as a matter of course, some mechanism for helping the well-trained teacher keep up with developments in his field of chemistry. In other words, retreading would become a normal and regular part of the academic life, and the traditional academic pattern may have to be modified to allow for this. Before discussing a possible change in this pattern, I would like first to comment on existing programs designed to help these teachers.

At present, most teachers undergo their academic retreading by attending summer conferences or special evening institutes. So far these have worked very well but I do not believe they can be regarded as permanent solutions to the problem. If the teacher of chemistry is not to carry an extra load as a regular thing, he must have some relief from his normal teaching load. This could be accomplished by lightening teaching responsibilities during the year or by granting him regular leaves-of-absence during his teaching career. For a number of reasons I am inclined to view the leave-of-absence goal as the one to aim at.

Refresher Leaves-of-Absence

My comments here would be very brief if it were standard practice to grant all college and high school teachers leaves-of-absence at regular time intervals. But this is certainly not the case. If serious study were given to the problem, I suspect that it would be found necessary to grant teachers a one semester's leave of absence at least every three or four years for the purpose of refresher programs of study. I have intentionally avoided the traditional academic term "sabbatical" in referring to leaves-of-absence for chemistry teachers. For one thing I believe the seven-year spacing of leaves is too great for the purpose of refresher programs: and for another, the tradition of the sabbatical year has its roots in early religious observances and carries with it the idea of almost complete idleness. Though no one would begrudge chemistry teachers the same opportunity for relief from teaching responsibilities that other teachers enjoy, the refresher-leaves I have in mind would not be for that purpose.

I have not attempted to estimate the expense of a continuing program of refresher-leaves-of-absence, but

it is certain to be very large. I venture to suggest, however, that it may not be the most expensive way to keep this country's teachers of chemistry reasonably well prepared during the next forty year period.

There is one further observation I should like to make concerning refresher courses for teachers on leaves-of-absence. I believe these courses should be special courses taught for the sole purpose of helping a group of experienced teachers. The general pattern of courses developed in the NSF program of conferences and institutes would be an excellent model to follow. I stress this point because I am convinced that it would be a serious mistake to utilize regular graduate courses for refresher purposes. This might not be good for the graduate course and it would generally be a rather inefficient use of the teacher's time. The best arrangement, probably, would be for several universities and colleges to include refresher courses for chemistry teachers in their regular curriculum offerings, in chemistry. Whatever the ideal method for helping the chemistry teacher—whether it is the leave systems I have mentioned or some other—it will not come about overnight. There is no practical alternative to starting with things as they are and attempting to improve the situation one step at a time as the opportunity to do so presents itself. I would therefore like to propose certain immediate steps which have occurred to me in the hope that this will lead others to come forward with other ideas.

My first suggestion has to do with the existing special training and refresher programs of all types. Although these programs offer the best approach at the present time to the general retreading problem, it is my opinion they have not been exploited fully. One difficulty perhaps, has been the fact that they operate on a year-to-year basis. Further, since these programs have been regarded more or less as trial runs with a probationary status, the directors of the programs have naturally selected the more capable applicants for their courses. It seems to me, however, that it might be desirable now to change the basis of selection and try deliberately to bring into these programs more of the older teachers and more of the less well prepared of the younger group of teachers. I use the phrase "try to bring in" because there will always be a group of teachers who will be reluctant to make the necessary sacrifice and who will have to be persuaded of the value of attending a refresher institute. If we want to improve the teaching of chemistry uniformly across the country, it may be necessary for the Society, preferably through our Division, to call to the attention of college and school administrations the opportunities currently available to their chemistry teachers and to ask them to encourage these teachers to take advantage of them.

Needed: Published Reviews of Developments

My second suggestion pertains to the do-it-yourself method of retreading which, after all, is the method most teachers have had to employ in the past. One problem which the interested but busy teacher faces is the selection of reading material in which to invest his limited time advantageously. For many years now we have had, for the research chemist, annual reports and reviews of developments in special areas of chemistry. These are not particularly helpful to the high school and college teacher. Possibly what is needed from the teachers' standpoint is an annual summary of broad trends and developments rather than complete coverage of a given field.[9] The kind of summary I have in mind would list, as a matter of course, all pertinent general articles which had appeared in our own JOURNAL OF CHEMICAL EDUCATION, the *Scientific American*, *Endeavor*, and similar publications. The time might come when the summary would include reprints of some or all of these articles, to make them more convenient for the busy teacher. The JOURNAL OF CHEMICAL EDUCATION has already experimented in this direction with very promising results.

In conclusion, there is one further suggestion I would like to make. I believe it would be very desirable for some office of our Society to address a letter to all new teachers of chemistry, both in high school and college, and alert them to the problem they face in keeping up with developments in chemistry. The letter I have in mind would inform the teacher of the various aids which are available to him and would also urge upon him the importance of taking advantage of these aids. I realize that the preparation and distribution of the letter I am suggesting would be an enormous administrative task, but I believe it would pay in the long run. Even in the matter of retreading, an ounce of prevention can be worth a pound of cure.

[9] The several symposia presented at the Cleveland Meeting sponsored in part by the Division of Chemical Education, were excellent summaries of "trends and developments." I am pleased to learn that the material presented in these symposia will be published in the JOURNAL OF CHEMICAL EDUCATION and made available to those who were unable to attend the meeting.

Chemistry for Elementary School Children

MCA's superb collection of "explorations" entitled "Matter, Energy and Change" belongs in the library of every chemist who has a concern for the science education of future generations.

Following the pattern so successfully established by MCA's "open ended" experiments for high school chemistry laboratories, there are six sets of experiments for kindergarten–third grade (materials, changes, air, water, plants, and the candle) and six for grades four–six (matter, reactions, electricity, chemical tests, crystals, and photography). Appendix I is a glossary; appendix II discusses the periodic law but supplies no table; appendix III is a helpful list, "Books about Chemistry for Teachers and Children."

Copies are available from Holt, Rinehart and Winston, Inc., 383 Madison Ave., New York 17, N. Y., at 50 cents a copy, four or more copies 40 cents each.

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Laboratory Safety

I. *Accident prevention*

In this series of three articles, laboratory safety at the high school, college, and university level will be discussed. The first article will deal with accident prevention, the second with specific problems of flammability and toxicity of commonly encountered compounds, and the third with emergency procedures designed to mitigate the effects of accidents when and if they do occur.

We firmly believe that safer chemical laboratories are feasible, as the record of the chemical industry has adequately demonstrated (*1*); that the teacher has both a moral and a professional responsibility to operate his laboratories safely and to train his students to work safely (*2*); and that good chemistry teaching and proper laboratory technique are inseparable from the teaching of safety in the laboratory and from safe laboratory procedure.

The Teaching Laboratories

To begin with, we must realize that students, being students, make safety in the elementary laboratory more of a problem than it is in the upper level or industrial laboratory. Students are inexperienced and unskilled; they cannot foresee the difficulties which experienced chemists avoid automatically.

Design of Laboratory Experiments

Most accidents in the student laboratory can be avoided by careful planning of what the student is to do. Safety must be designed into the laboratory experiment. Experiments must teach, but they do not have to be dangerous to make their point. Thus, safety should be considered along with cost, ease, and reliability in selecting an experiment. For example, if the student is to study the reaction of an active metal with water, several metals might be chosen. Sodium is an obvious choice, but calcium and sodium-lead alloy (*3*) also react smoothly with water, evolve hydrogen, and leave behind a solution basic to litmus. The hazards of metallic sodium are well demonstrated (*4*). Both sodium-lead alloy and calcium are easier to handle and react less violently with water than does sodium and, using these metals, the student sees the same chemistry but at less risk.

Checking Laboratory Experiments

Many teachers have no opportunity to design their own laboratory experiments since the choice of experiment is made by the teacher's supervisor or by the author of the laboratory manual. Under these circumstances, the teacher must try everything first. During the preliminary discussion of the experiment, he can then point out the interesting chemistry and can also caution the class about the hazards involved.

There are two ways to mention safety. Either the teacher can point out directly, with definite do's and don't's, the problems to be encountered or he can take a more positive approach and demonstrate the proper way to perform a particular operation. For example, directions for preparation of dilute acid solutions may include the emphatic statement, "Always pour the acid into the water or everything will blow up in your face," or more gently, the proper way can be demonstrated, several students can tell the class how hot the beaker becomes, and this can be followed by the statement, "Since concentrated acids react with water with the evolution of heat . . . ." The class may then be asked to reach conclusions as to the hazards of pouring water into concentrated acids. The choice of methods will depend upon the nature of the class but, in general, the second method is preferable. The emphasis is now upon the operation and the principles and no attempt is made to scare the student into safe behavior. (A scared student is himself a hazard.)

Adequate Student Preparation

An effective means of minimizing careless mishaps is to insist on careful student preparation. One method requires the student to submit a brief written statement before he can exercise the privilege of experimenting in the laboratory. A half sheet of paper can contain (*a*) the purpose of the experiment or the nature of the problem to be investigated, (*b*) the student's plan of attack on the problem, and (*c*) the objectives the student hopes to attain as a result of the exercise. This procedure allows the laboratory assistant to check the student's plans and enables him to point out, and suggest means of avoiding, difficulties.

Control During the Experiment

Each laboratory experiment has its own set of peculiarities and idiosyncrasies, most of which will be caught by the teacher as he works through the experiment himself. However, some difficulties appear only when a class attempts the experiment. Small matters of technique, used automatically by the experienced teacher, will probably not be used by the inexperienced student.

For example, when the experienced teacher demonstrates the correct method for preparing sulfur dioxide gas, he will keep the end of the delivery tube close to an operating hood. However, when the class attempts the same experiment, several students will probably work out on their bench tops, well away from

the hood system. The teacher should then stop the laboratory work, call the class's attention to the error, and then allow them to continue. A brief note in the teacher's own manual will recall the incident to mind in time for the preliminary discussion for the next class.

Again, students often err when heating a test tube or a flask by pointing it at another student. Excessive and improper heating, by concentrating the heat on the bottom of the test tube, will cause the solution to spew forth and perhaps injure neighboring students. While the experienced teacher automatically points the test tube toward a blank wall or the ceiling when heating, the student will not be aware of the effects of superheating and always needs several reminders to avoid danger.

There are numerous safety devices, ranging from the rags used to protect the hands during the manipulation of glass tubing to the most expensive controlled-air-flow hoods for handling radioactive materials. These safety devices augment the properly designed experiment, aid both the experienced and inexperienced laboratory worker, and mitigate the effects of accidents which are bound to happen no matter how thoroughly the class has been trained.

In the high school and undergraduate teaching laboratories, where large numbers of students are handled, it is necessary to balance the desirability of a particular safety device against the expense involved in supplying it to the class. Examples chosen from one of our laboratories will illustrate this point.

Two types of accident occur frequently in the undergraduate (freshman) laboratory: cut fingers and hands caused by breaking glassware and eye injuries caused by splashing chemicals. The simple requirement of having students wrap their hands in towels before manipulating glass tubing decreased the number of cuts appreciably. Readily available bottles of glycerine to act as lubricant also helped. The cost was small, the results good.

It is now a course requirement that some form of eye protection be worn by everyone at all times in the laboratory. Ordinary eyeglasses or clear plastic safety glasses are acceptable. This requirement has been partially responsible for reducing the serious eye injuries in the qualitative analysis laboratory by roughly 75% over the past three years. Perhaps 60% of our students have had to pay $1.75 for their personal pair of plastic safety glasses. This is a small price to pay to prevent injuries to an estimated fifteen pairs of eyes.

As expected, persuading the student to use the safety devices provided is a major problem. Constant reminders, both by the lecturer and the laboratory assistants, have proved successful.

The neat, uncluttered laboratory will have fewer accidents than the cluttered, sloppy laboratory. Spilled chemicals are unsightly, indicative of poor laboratory technique, and a real hazard; chemicals stored in the laboratory are too easily available for unauthorized experiments, may be spilled or knocked over accidently, or may become involved in a small fire and contribute to the severity of the blaze; narrow and cluttered aisles prevent the easy access of the teacher to the student and may cause passing students to interfere with the working areas of others; poor lighting, equipment in poor repair, and inadequate hoods and wiring also pose safety problems.

Unfortunately, there is often very little that the teacher can do about the overcrowded, cluttered laboratory. Laboratory space is limited and will become more limited in the future. In the crowded laboratory it is doubly important the the teacher insist that the students keep the laboratory orderly by cleaning up all spilled chemicals, discarding all broken or chipped glassware immediately, and disposing of used chemicals properly.

Discipline in the laboratory is also an important part of laboratory safety. Most students, fortunately, are willing to accept suggestions that will prevent injuries to themselves or to their friends. Horseplay, careless handling of chemicals, removing chemicals from the laboratory, and any unauthorized experiments must be forbidden. A "professional," purposeful atmosphere in the laboratory will influence the student to keep his mind on what he is doing.

Special Projects

Here we include science fair exhibits, chemistry club activities, special help or advanced sections, and all other extracurricular use of the teaching laboratories. Experiments and exhibits should be designed carefully, and each proposed experiment read through and checked thoroughly by the teacher before the student is allowed to go into the laboratory. Careful supervision by the teacher should be exercised and the use of safety devices required.

Almost every chemistry student at one time or another wants to make gunpowder, a rocket propellant, or perhaps nitrogen triodide. Unless the teacher is a qualified expert in explosives, unless there are properly designed facilities for the preparation and testing of these materials, and unless the teacher is ready to assume the moral responsibility for student injuries, experiments with explosives, rocket propellants, or shock-sensitive compounds should be strictly avoided. Amateur rocketry in particular is extremely dangerous, serves no purpose scientifically, and should be firmly discouraged. There are too many good, exciting, scientifically sound, and significant projects which can be done at the high school and undergraduate college level to waste time and risk injuries searching for the bigger and better bang.

For other comments concerning amateur rocketry and the tendency for students to play with dangerous chemicals, references (*5–8*) should be consulted.

Lecture Demonstrations

The lecture demonstration is an integral part of most elementary chemistry courses, since some important experiments require more skill than the student possesses; others require more equipment than the student has available; still others are too hazardous for an untrained person to perform. It is this last type of demonstration which presents an obvious hazard, as witness the explosion of aluminum powder and liquid oxygen during a demonstration lecture (*9*).

The same rules apply for lecture demonstrations (both the obviously hazardous and the seemingly innocuous) as apply to general laboratory safety. First, choose the least hazardous experiment that will make your point. Second, work through the experiment carefully before attempting the demonstration before a class. Finally, assume that something may go wrong with the experiment and design your experimental set-up accordingly. A demonstration involving flammable liquids done without a fire-extinguisher handy or a reaction evolving noxious gases conducted outside an adequate hood is a foolhardy endeavor.

The Research Laboratories

Until recently, the high school and undergraduate college teacher was not involved in research, and the safety problems of the research laboratory were not his to worry about. However, there is now a definite tendency toward research even at the high school level. Science fair projects, chemistry clubs, and advanced chemistry course work, aided by the increased availability of research grants, have put many teachers into research activities. Therefore, the following discussion of safety in the research laboratory will be almost as pertinent to the high school or college teacher as to the university research man.

The research laboratory is a high hazard area. The flammability and toxic properties of new materials are unknown; the use of high pressure and high vacuum systems, complex electrical circuits, and radioactive materials adds to the dangers. Further, the undergraduate and first-year graduate researcher are novices in research. The responsibility of the research advisor is nowhere more evident, nor can the example set by the more experienced research student be more telling, than in the area of accident prevention.

It is impossible to consider all the hazards to be encountered in any particular research laboratory, and this discussion of accident prevention will have to be general rather than specific. References given after each section heading should be consulted for further information.

General Rules (10–13)

Laboratory work should never be done by an isolated researcher. A colleague must always be within hearing distance and should be informed if any particular work is known to be extra hazardous.

Safety devices such as safety glasses, face shields, gloves, fire extinguishers, and gas masks should be readily available to every research man.

New reactions should be run on a small scale and then scaled up with caution.

Good housekeeping is a must in the research laboratory. A working laboratory is usually a bit sloppy, but an occasional (monthly?) general clean-up of old chemicals, a straightening out of reagent shelves, and the return of unneeded chemicals to the stockroom will go far to prevent accidents and mitigate the effects of accidents which do occur.

Sometimes things go wrong during a reaction and accidents happen. Usually, a reaction about to go out of control will give some warning: a sudden unexpected rise in temperature, appearance of fumes, or a cracked flask or reflux too high in the condenser. Do not try to be a hero. Beat a hasty retreat, take cover, and warn your laboratory companions. From a safe distance, size up the situation and then take the proper steps—long fast ones to the nearest exit if that seems appropriate. Protection of yourself and others in the laboratory is your first duty.

No set of rules or elaborate safety devices will ever take the place of care and foresight in the design and manipulation of any experiment.

Flammable Materials (14, 15, 16)

The general use and storage of flammable materials in the research laboratory is a hazard. The best time to consider the nature and extent of this hazard is before the materials become involved in a fire. Sources of information concerning the common flammable materials are listed in references (*17*, *18*) and a more detailed discussion of flammable materials will appear in Part II of this series of articles. Certain general rules for the storage and handling of flammable materials will be considered here, however.

The common, and extremely hazardous, practice of using glass bottles for laboratory storage of flammable materials should be avoided. Glass containers break easily, either through careless handling or when involved in a fire. Vapors from a broken container will ignite at any convenient source of heat and will either cause a fire or add to the severity of a fire already started. Underwriters Laboratories or Factory Mutual approved safety cans with flame arrestors in place are more expensive, but much safer, than glass bottles for the laboratory storage of flammable materials. All containers should be carefully and prominently labeled.

The quantity of flammable materials in any one laboratory should be kept to the minimum necessary for the type of work done in that laboratory.

NEVER store flammable liquids in an electric refrigerator unless the refrigerator has been especially wired to insure that no sparks will occur when the thermostat operates, the light lights, or the door closes. Ordinary household refrigerators, unmodified for safety, have been the cause of many unnecessary fires and explosions.

Be sure that all sources of ignition (burners, hot plates, lighted cigarettes, etc.) are removed from the area before transferring flammable liquids. Vapors will travel many feet from their source to an ignition point.

The flow of non-conducting liquids through a pipe or the pouring of these liquids from one container to another may create enough static electricity to produce a spark and cause a fire. Ground all containers before pouring.

Water-immiscible flammable liquids should never be poured into the sink. These flammable liquids may accumulate in the sink traps or be spread through the sewer system and a stray spark will lead to a widespread fire. Local ordinances usually prohibit the introduction of flammable liquids into the public sewer system.

Toxic Materials (Including Radioactive Materials) (19, 20, 21)

Adequate hood systems, proper safety devices such as gas masks, respirators, gloves, and goggles, and the consistent and proper use of these safeguards are the best means for preventing accidents due to toxic chemicals. The subject of toxic materials will be treated in greater detail in Part II but again, some general rules may be given.

Volatile, toxic materials must be handled, and usually stored, in the hood. It is not sufficient that the material be in the hood—the hood must also work properly and efficiently. Hoods should be checked regularly and according to a prescribed schedule. Repairs must be made immediately on any poorly operating hood system.

Always know the countermeasures to be taken if an accident should occur. The best time to secure this information is before the accident happens. The labels on bottles of chemicals will often list an antidote for the chemical. Remember also, the physician called in to treat the effects of an accident probably knows little about the effects of or the countermeasures necessary to control a particular toxic material. The research man must be able to supply the necessary information quickly.

Do not taste chemicals or pipet by mouth.

Radioactive materials present a high toxicity hazard. Ingestion of radioactive material is a particularly great danger and adequate, specially designed hood facilities, the use of personal protective equipment, such as gloves and respirators, and the extreme in personal cleanliness are necessary to prevent accidents.

Electrical Equipment

The Underwriters Laboratories label on a piece of electrical equipment is a good guarantee that the equipment is safe, if properly used. Some rules for the proper use of electrical equipment are:

Equipment which produces even the slightest shock should be disconnected, checked, and repaired immediately.

In repairing electrical research equipment, disconnect the apparatus, ground out any accumulated charges on condenser plates etc., and wrap tape around the plug so that a helpful visitor will not plug in the apparatus while your fingers are still inside.

Repairs to laboratory electrical lines, outlets, and switches should be made only by an authorized electrician, never by the research man himself.

Not only is electrical equipment a life hazard, but it is also a major cause of laboratory fires. Of 100 laboratory fires studied by the Fire Record Department of the National Fire Protection Association, 21 were caused by faulty or improperly used electrical appliances or wiring. This record may be compared with the 20 fires caused by improper use of flammable liquids or the 13 caused by miscellaneous explosions.

"Electrical mishaps cause the greatest number of laboratory fires. The worst of these fires break down into two groups: (1) the wiring group and (2) the thermostat group."

"The wiring group is responsible for fires mainly because of the temporary nature of many laboratory experiments. The NFPA National Electrical Code (No. 70) will provide reasonable protection against wiring faults."

"The thermostat group of fires is due to reliance on a single thermostat. Any thermostatically-controlled device in which failure of the thermostat to shut off would cause overheating should be equipped either with a fail-safe circuit or with a secondary, high temperature cutoff thermostat. Thermostats used when flammable vapors, gases, and combustible dusts are present should be of a type designed for use in such hazardous locations." (*22*)

Vacuum Equipment

There are three general hazards connected with manipulations carried out at reduced pressures: implosion, "bumping," and mercury poisoning.

Implosions can often be prevented by proper design of equipment and by careful manipulation. All equipment used in vacuum work should be free of cracks and scratches; any seals should be of uniform wall thickness and thoroughly annealed; sharp angles are to be avoided. The effects of implosions can be guarded against by setting up safety shields around the apparatus, wrapping the apparatus with wire mesh, and wearing a full face shield when operating equipment under vacuum. Dewar flasks and vacuum desiccators are potentially hazardous and should be adequately shielded or wrapped with tape.

"Bumping" during vacuum distillation sets up stresses in the apparatus which may lead to an implosion or may carry material over into a portion of the apparatus where its presence is not desired. A dry-nitrogen leak down into the material to be distilled will help avoid severe bumping as will careful and gentle manipulation of stopcocks on a vacuum chain. Boiling chips are almost worthless in vacuum distillations.

Since mercury seals, pressure relief valves, and manometers are components of most vacuum systems, extreme care must be exercised to avoid mercury spills and inhalation of mercury vapor. Traps should never be filled more than one-third full of mercury. All mercury containers should be supported securely and a beaker or pan placed underneath to catch spilled mercury. Although the hazards of large pools of mercury should not be discounted, the primary hazard arises from small droplets which are widely dispersed in cracks in benchtops or in the floor of the laboratory. A light dusting with flowers of sulfur will coat the surface of these particles of mercury and help reduce the concentration of mercury vapor in the air of the laboratory.

Compressed Gases (23–26)

The heavy metal cylinders containing compressed gases are potential health and fire hazards. Be careful in moving, storing, and using these cylinders.

Properly designed hand carts must be used to transport cylinders. The cylinders are too heavy and awkward to risk manhandling.

The threaded connection holding the valve assembly to the tank is the weakest point in the system. A sudden stress applied to this point, as might occur if the cylinder tips over, will snap off the valve, release the gas, and propel the cylinder rocket-like through anything in its path. Keep the protective cap in place when the valve is not in use, and be sure that all cylinders, always, are strapped securely to a firm support.

Be sure that you know what gas you are using. Labels, color codes, etc., should be checked carefully. Serious accidents have occurred when oxygen gas was accidently admitted to a system instead of the desired nitrogen.

Use the proper reducing valve and do not attempt to interchange valves from one gas service to another. Reducing valves cut down on the pressure applied to a system and permit more precise pressure control. (Control of gas pressure solely with the tank valve is almost impossible.) Also, reducing valves accumulate small quantities of the gas which passes through them or react slightly with this gas. Use of a contaminated valve with another gas may cause a violent reaction.

If the gas is being fed into a system containing liquid, place a reservoir large enough to hold all the liquid in the system between the cylinder and the reaction vessel. This reservoir will prevent suck-back of liquid into the cylinder due to pressure fluctuations.

All pressure systems must have a pressure relief device to prevent dangerous pressure build-up.

If a cylinder becomes involved in a fire, the safety pressure relief disk in the valve assembly is likely to rupture and release the contents of the cylinder. Should this occur with a cylinder of flammable gas, do not attempt to extinguish the flame at the valve. Cool the cylinder with a fine spray of water, allow the gas to burn off, and protect the surrounding area from the heat of the flame. If the safety disk has not ruptured, cool the cylinder, extinguish the flame, and close the valve. Explosions in LP (liquid propane) gas cylinders have occurred as flame impinging on the cylinder weakens the metal. Cylinders of compressed gases when involved in a fire must be kept cool with water spray.

Planning Laboratory Safety (27–30)

Ideally, every school—high school, college, or university—would have a continuing program designed to spot and eliminate hazards in its laboratories. This program would also train students and faculty in the use of such safety devices as fire extinguishers and gas masks, disseminate facts concerning safety, and see to it that the proper safety devices are available where needed. In establishing such a program, the following suggestions may be helpful.

The need for a program must be recognized—preferably before a serious accident points out the need for laboratory safety.

Some one individual should be willing to take the responsibility for the program. "Safety committees" are excellent means for informing laboratory people about safety and for spotting particular hazards, but there must be a responsible leader.

The safety status of the department should be determined and the particular hazards spotted. Safety manuals and pamphlets (*25, 29, 31*) will help in defining these hazards. The number, type, and state of repair of fire extinguishers, gas masks, etc., should be included in this survey.

Clean up the obvious hazards immediately. Sloppy housekeeping, excessive storage of flammable liquids, unsupported gas cylinders, and unshielded vacuum equipment can be eliminated with a minimum of expense.

Determine the number and kinds of safety devices which must be added to protect against the hazards which exist within the laboratory. Fire extinguishers, gas masks, and first-aid kits are expensive; so set up a priority list, and concentrate attention on those items of most pressing need.

Start the safety education program.

Safety Education

The goal in safety education is to have every faculty member (and graduate student) trained to work safely and prepared to meet any emergency situation with speed, correctness, and confidence. Keep in mind, however, that discipline in an educational institution differs from military or business discipline. You must proceed with tact and diplomacy.

Emphasis must be positive, indicating the proper, correct, and safe procedures to be followed in all laboratory operations or when confronted with an emergency situation. Too heavy stress upon the horrors associated with laboratory accidents or graphic descriptions of gory injuries or nasty fires should be avoided. Particularly with high school and college undergraduate students, do not frighten the student so badly that he is "scared to death" to walk into a laboratory or to perform the simplest laboratory experiment. Frightened, timid students are more likely to have accidents than the confident laboratory man who works with due regard for safety.

Safety information from such sources as those listed in the Literature Cited section should be placed in the library and its presence and utility described in a memo to the faculty and graduate students. A short lecture to the incoming students (particularly the teaching assistants) in which safety rules are discussed and safety equipment demonstrated may be helpful. If possible, allow the student to extinguish a small fire and try on a gas mask. The fire department will help here. Memos or short safety manuals (*31, 32*) concerning the use of safety equipment and proper laboratory procedure can be distributed in intervals within the department. Discussions and demonstrations of safety procedures can be worked into an existing seminar program. Safety hazards can be brought individually to the attention of the graduate student and faculty member as they are observed. (Caution: some faculty members and graduate students, like some chemicals, are explosive if treated incorrectly. Use tact and good judgment.)

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Alkaloids—the World's Pain Killers

Among the vegetable products, numerous oily or crystalline bases have been found to which the term "alkaloid" has been applied, and because of their physical properties, they have for ages past interested mankind.

When the orientals used opium or hashish, or the South American natives chewed the coca leaves for stimulation or the cinchona bark for fevers, they did not know that the reason they obtained results lay in the alkaloidal content of the material. Only within the last few decades has the organic chemistry of certain alkaloids been expanded. Due to the complex structure of the alkaloidal molecule, a study of the chemistry of the alkaloids is one of the most difficult fields of organic chemistry and even today the structural formulas of many important drugs are still more or less uncertain.

It is difficult to formulate an exact definition of an alkaloid. The definition may be made so broad as to include all nitrogen-containing compounds or so narrow as to leave out compounds with definite alkaloidal properties. Ladenberg originally defined them as "those naturally occurring vegetable substances of a basic character which contain at least one nitrogen atom forming a part of a heterocyclic ring." If we except the purine and pyrimidine bases, we can limit the definition to basic substances found in plants and which contain a cyclic nitrogenous nucleus. Even this is too narrow, for a few compounds do not contain a cyclic nitrogenous nucleus; nevertheless, they may have the marked physiological properties of alkaloids. The modern chemist may well take exception to the words, "naturally-occurring." Synthetically medicinal substances have been prepared which are better than the naturally occurring alkaloids, and these synthetic products are truly alkaloidal, both in chemical and physiological properties, if we accept chemical and physiological properties as criteria of alkaloids. No definition, accordingly, can be completely satisfactory. Ladenberg's definition is only satisfactory when applied to those alkaloids which occur in nature.

Historically, the work on alkaloids dates back to 1803 when Derosne isolated a crystalline compound from opium, which he called "opium salt." He did not, however, notice its basic character. In 1805, Serturner, a German apothecary, isolated the material again independently, purified it, recognized its basic properties, and called it "morpheum." At the same time he separated an acid which he called "meconic" acid and expressed the view that the two were combined in opium. These observations remained unnoticed until 1817 when Serturner published a second paper in which he further pointed out the basic character of morphine and described a number of its salts. Chemists then began to look for other similar compounds, and in 1818, Pelletier and Caventou found strychnine in Nux Vomica, followed by brucine in 1819, and in 1820 they isolated quinine and cinchonine from cinchona bark. At least two or three new alkaloids have been isolated and described each year since 1820.

There was considerable speculation by the early chemists as to the chemical constitution of these compounds, but the first definite clue was obtained about 1842–6. Gerhardt, in 1842, distilled quinine, strychnine, and cinchonine with solid potassium hydroxide and obtained an oily base which he called "quinoleine;" later the name was changed to quinoline.

Previous to this, Runge (1834) had obtained a base from coal tar which he called "leucol," and Hoffman found that "quinoleine" and "leucol" were identical. Meanwhile, Anderson (1849–51) separated pyridine from bone oil, and later this base was isolated from nicotine, coniine, and piperidine by distillation with zinc dust. Isoquinoline was isolated from coal tar in 1885 and was later obtained from two other alkaloids, hydrastine and papaverine. The fact that coal-tar bases could also be obtained from alkaloids stimulated research, and by breaking down alkaloids on the one hand and building up derivatives of the coal-tar bases on the other, points of contact were established and information regarding the alkaloidal molecule was obtained. Eventually, some of the alkaloids were synthesized, and the recent advance in this field has been in the discovery of the potent groupings and the use of these new groupings in new compounds which are better than the naturally-occurring alkaloids, in that they have the same curative or medicinal properties and fewer of the undesirable properties.

Many alkaloids are of great commercial importance and are prepared on a large scale: morphine, codeine, quinine, nicotine, strychnine, and cocaine. The procedure varies with the physical and chemical properties of the desired base, and the utmost advantage is taken of solubility in alkali or specific organic solvents of salts, so that only general methods can be given. The dried and powdered plant parts are extracted with water, alcohol, or dilute acids, and the crude mixed alkaloids precipitated with ammonia or other alkalies. The individual alkaloids are then separated through differences in the solubilities of their salts. The final step in purification is usually the removal of coloring matter by heating solutions of the salts with finely divided charcoal or by passing the solutions through

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activated charcoal treating beds. Sometimes the plant material is digested first with alkali, and the water-insoluble alkaloids then extracted into benzene, chloroform, or other suitable solvents. With volatile alkaloids, as nicotine, steam distillation may be employed. Most alkaloids are obtained from the natural sources, but a few, such as ephedrine and papaverine, are synthesized commercially.

Before considering the chemistry of the alkaloids, it is perhaps justifiable to note certain families of plants in which the alkaloids occur. Alkaloids are distributed throughout the various groups of the plant kingdom. In some families of plants many alkaloids are found. Other families are noted by the particular absence of the materials. Very few of the monocotyledonous plants contain alkaloids, these compounds being confined almost exclusively to the dicotyledonous plants. Among the angiosperms there are several plants which are noteworthy for their alkaloidal content: "dogbane," legumes, poppies, buttercup and crowfoot, madder, potato, tomato, and Nightshade.

Other families, such as the mints, roses, orchids, etc., sometimes, though rarely, contain alkaloids. They may occur in leaves (coca), cell sap (opium), stems, seeds (nux vomica), fruits (piperine, black pepper), bark (quinine), or in roots (berberine in barberry roots). Rarely does one alkaloid occur alone, usually two, three, or more occurring together; opium contains some 20, and new ones are still being isolated from it.

The alkaloids are usually solid and crystalline, but a few, like nicotine and coniine, are liquids. They are mostly colorless, although a few are yellow. They rarely occur free in the plant tissue, but rather as salts of organic acids, e.g., malic, citric, succinic, oxalic, etc. In a high vacuum, some of the complex alkaloids may often be sublimed or distilled on a small scale as in the case of strychnine. Alkaloids readily form crystallizable salts with inorganic acids and are extracted from plant tissues by dilute sulfuric acid or hydrochloric acid. Certain of the alkaloids are volatile and may be steam-distilled from alkaline media; the non-volatile ones are set free by sodium hydroxide and extracted with ether, chloroform, or other reagents. Most alkaloids are bitter, but this is not a necessary property, for piperine, from black pepper, is tasteless. Most of the alkaloids show characteristic absorption spectra, and this property is used in determining the composition of some of the more complex alkaloids.

Alkaloids are active ingredients of many drugs used for pleasure or stimulation; coffee, tea, cocoa, coca leaves, tobacco, betel nuts, mescal or the "big drunk bean." Marihuana, however, contains no types of known alkaloids. A few alkaloids are used as pest exterminators, but the main use is in the field of medicine.

Almost all the alkaloids are extremely poisonous to animals and insects, while strangely enough, this same property may aid in the survival of the plant species.

The remainder of this paper will discuss three important examples of alkaloids and their specific uses.

Morphine, an Opium Alkaloid

Opium is the dried exudation of the Papaver somniferum, a poppy which is grown in India, Turkey, Egypt, and Peru. The principal supply in the United States comes from Turkey, largely due to the fact that opium grown in Turkey meets the requirements of the USP. The common red field poppy yields some opium but is generally considered too little to be commercially attractive.

Opium has been used from the earliest times. It was mentioned by Theophrastus in the third century, B.C. Galen, a famous physician of the second century, A.D., spoke highly of the virtues of opium. Laudanum (tincture of opium) was originated by Paracelsus (1493–1541). Powder of ipecac and opium (Dover's powder) was first compounded and used as a diaphoretic by Thomas Dover, an English physician and pirate, in 1782. Although now much restricted in use, opium is still of great value in medicine. Crude opium contains 20 or more alkaloids; the most important are: morphine, 10.0%; papaverine, 1.0%; codeine, 0.3%; narcotine, 6.0%; thebaine, 0.3%. The active principles of opium were isolated during the first half of the nineteenth century. Morphine, the principal alkaloid of opium, was isolated by Serturner in 1805. When Serturner first presented his morphine to the chemical world, its importance was recognized by many who tried to take the credit for his discovery. For 36 years, Serturner tried in vain to prove his discovery, but at the age of 57 he began to suffer with terrible pain, the pain he had conquered so brilliantly for others. He was barred from the benefits of his own morphine, however, since he had become so weak that he could not swallow it and there was no hypodermic needle then which could have quieted him in his last days. One of the benefactors to humanity, the man who turned treacherous opium into pure and reliable morphine, who started doctors on the way to use pure drugs, died forgotten and friendless in 1841.

Most factory processes for the isolation of morphine are based on the Robinson-Gregory method. A concentrated opium extract is treated with calcium chloride which precipitates the calcium salts of meconic, lactic, and sulfuric acids. On concentration of the liquid portion, the double salt of morphine and codeine hydrochlorides crystallizes. It contains about 20 parts of morphine to one of codeine. These are separated by treatment with ammonia in dilute solution which precipitates the morphine and leaves the codeine dissolved.

Morphine has the formula $C_{17}H_{19}NO_3$, and the nucleus is of the isoquinoline-phenanthrene type. It crystallizes in fine, colorless rhombic prisms, as a monohydrate. The anhydrous base melts at 254°C with decomposition. It is soluble in cold water about 1 part in 10,000, in boiling water, 1 in 500, sparingly soluble in ether, alcohol, or chloroform. The water solution is bitter and reacts alkaline. The alkaloid and its salts are levorotatory in solution. A large number of salts of morphine are known; in medicine the most common are the hydrochloride, sulfate, hydrobromide, and nitrate. They are all quite similar in action and all very poisonous. Many tests have been devised for the detection of morphine. Only a few can be listed: concentrated nitric acid, intense orange-red; ferric chloride solution, deep blue, destroyed by excess acid; formaldehyde in concentrated sulfuric acid, violet-red. Numerous derivatives of

morphine have been made; the most important are codeine, ethylmorphine, diacetylmorphine, dihydromorphine, and dihydromorphinone. Like morphine, all are habit-forming and cause addiction on prolonged administration. This addiction is such a serious social problem that the sale and possession of morphine is strictly controlled in the United States, originally under the Harrison Act passed in 1914, and in present form enforced by the Bureau of Narcotics, Treasury Department.

Morphine and its derivatives are of great importance in medicine and surgery because of their power to control pain. They also have less desirable actions, such as emetic effects, slowing of respiration and heart, and depression of intestinal activity.

When first used, morphine was the only good "pain killer" and therefore it was used for all types of pain and disturbances such as ulcerations, consumption, stomach-ache, headache, dizziness, sore throat, tuberculosis, syphilis, goiter, and at least four types of pip. So it can readily be seen that morphine has come a long way in the field of chemistry and medicine.

Strychnine, a Quinoline Alkaloid

Strychnine, $C_{21}H_{22}N_2O_2$, is an alkaloid obtained from seeds of Strychnos nux vomica, a small tree grown commercially in China and the East Indies. The grayish disc-shaped seeds of nux vomica were known to be poisonous as early as 1640. Records show that the seeds were used to destroy crows, pests, stray dogs, etc. These seeds yield several alkaloids, principally strychnine and brucine, of which strychnine is the most important. The alkaloid, strychnine, which was isolated in 1820, has largely supplemented the whole drug for medicinal purposes. Strychnine was at one time one of the most frequently used drugs, either as a preparation of the drug or as the alkaloid, but it is now less frequently used. Osler once said that he "practiced medicine with hope and nux vomica." Contrary to Dr. Osler, although strychnine is an interesting drug, it is used to a limited extent in present-day medicine.

Strychnine increases the reflex excitability of the spinal cord and the medullary centers but has little effect on the centers above the medulla.

Strychnine is quickly absorbed from the intestine. Following oral administration, after hypodermic, intravenous, or rectal administration, absorption is much more rapid. After absorption, strychnine is found chiefly in the blood, liver, and kidneys. The drug is destroyed chiefly by the liver, but about 25% is excreted unchanged, mainly in the urine. Urinary excretion starts soon after absorption and is completed in from 48 to 72 hours. When injected into the blood stream, 50% leaves the blood in five minutes.

The dominant action of strychnine is its ability to increase the reflex excitability of the spinal cord. Practically all reflexes are equally affected. Strychnine acts strongly on the spinal cord, less powerfully on the medulla, and slightly on the brain. Even weak doses intensify the irritability of the spinal reflexes so that weaker stimuli are effective.

The stimulation of the spinal cord is followed by depression and paralysis. The sensory part of the spinal cord seems to become paralyzed first, and then the motor cells, until stimulation elicits no action.

The special senses—touch, taste, smell, and hearing—are made more acute. The field of vision is increased and color discrimination is sharpened. Pain is more keenly felt. The heart is not directly affected by strychnine, although there may occur some slowing due to stimulation of the inhibitory center.

Convulsions due to strychnine may last one to two minutes followed by five to ten minutes' relaxation. Death occurs during a seizure due to fixation of the respiratory muscles.

Because of the intensely bitter taste of the salts of strychnine, they are taken orally in the form of the tincture or elixir as a "bitter" to stimulate the appetite and increase the flow of digestive juices. It is mainly absorbed by the intestine and after absorption it increases the movements of the bowel by its action on the muscle or ganglioplexus in the bowel wall.

Cases of strychnine poisoning are fairly numerous. Strychnine is the chief constituent of most gopher and rat poisons and as such has been a frequent source of poisoning. Cathartic pills containing strychnine are one of the most frequent sources of accidental poisoning in children. Strychnine is readily absorbed from the intestines and the symptoms appear in from fifteen minutes to an hour.

Strychnine is a good antidote for the treatment of narcotic poisoning which depresses the respiratory center and spinal cord. It is also used in acute and chronic alcoholism.

Curare, a Harnessed Poison

The lethal power of curare, a poison from the plant Chondrodeydron Tomentosum, was known to the white travelers in South America as early as the 16th century, but it was not until 1938 that Richard C. Gill, an American explorer, brought back quantities of curare and gave scientists a chance to discover its virtue.

Natives who polished off their enemies with curare-coated arrows, called the drug "flying death," but the doctors found refined curare valuable in relieving spastic paralysis and in relaxing muscles of the mental patients undergoing convulsive shock.

Now the jungle poison had a new use, as an anesthetic. After more than two years of clinical observations, Dr. Harold R. Griffith of Montreal reported that curare combined with cyclopropane, ether, or sodium-pentothal is safe when administered under properly controlled conditions. By paralyzing the junction between the nerve tissue and the muscle it controls, curare is said to produce the muscular relaxings required in prolonged operations to get rid of using large amounts of a gas.

Thus one has another glance at another alkaloid and its wonders. These three alkaloids are an example of the unity and yet the vast differences that mark the characteristics of the alkaloids. Today one of the largest fields in both chemistry and medicine is the field of "pain killers" and anesthetics, and the alkaloid's greatest contribution lies in this field.

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Determination of Alkaloid Structures

I. Isolation, characterization, and physical methods

There are several well-known books on the chemistry of the alkaloids (*1*), but these tend to discuss the detailed chemistry of particular groups of alkaloids. It is the purpose of these articles to outline the general methods of approach in alkaloid chemistry.[1]

The term "alkaloid" (alkali-like) is applied to the large group of basic nitrogen-containing natural products of vegetable origin. They are usually colorless (berberine is yellow), well-crystalline solids, but some from the tobacco, hemlock, and pomegranate root bark are liquids. The bases are usually optically active (mainly levorotatory) though a few such as coniine, cinchonine, laudanosine, pilocarpine, and pelletierine are dextrorotatory, and others like berberine, papaverine, and pilocereine are optically inactive. In most cases the nitrogen atom forms an integral part of a cyclic structure. Classifications of alkaloids usually exclude simple amines, purines, betaines derived from amino acids of proteins, choline, and other bases of biological importance which in contradistinction to the typical alkaloids are not limited to one or a few species of plants.

Alkaloids occur most abundantly in the higher orders of the plant kingdom and have been found in over 90 different families of flowering plants (*2*).

The majority of these families belong to dicotyledenous orders and the number of monocotyledenous families showing the presence of alkaloids is relatively small. The Gymnosperms and Pteridophytes are poorly represented and so far as is known alkaloids are virtually absent from the lower groups of plants with the exception of one or two families of the fungi (e.g., ergot) (*3*). Alkaloids generally occur in the plant tissue at points of intense cell activity such as the leaves, roots, bark, and seeds and are generally regarded as plant metabolic byproducts. There is considerable variation in the alkaloidal content in the plant depending on such factors as time of reaping and methods of cultivation and selection.

A knowledge of the botanical origin of an alkaloid can be useful in giving indications of the structural type of alkaloid which is likely to be present. Plants of the same family generally tend to produce alkaloids of the same structural type. This is a generalization which has to be applied with caution for there are alkaloids such as nicotine and berberine which are found in several different plant families. Also plants such as the opium poppy give a number of different structural types of alkaloids though the latter are probably biogenetically related.

Alkaloids occur usually as salts of the common plant acids. In certain plants, however, a specific acid may be found associated with certain alkaloids such as quinic acid in the cinchona group, aconitic acid in the aconitines, and meconic acid in the opium group. A few alkaloids such as narceine and narcotine are found free in nature, probably because of their low basicity. A few alkaloids as found in the solanum and veratrum groups occur as glycosides of such sugars as glucose, rhamnose, and galactose. Other alkaloids as in the

[1] The present article deals with methods of isolation and characterization and the applications of physical methods to the determination of alkaloid structures. The second paper, to be published in October, will describe chemical methods of structural determination.

Table 1. The Occurrence and Use of Some Common Alkaloids

Alkaloid	Source	Use	Alkaloid	Source	Use
Arecoline	Betel nuts	Masticatory; vermifuge	Morphine	Opium	Pain relief; narcotic
Atropine	Belladonna	Mydriatic in ophthalmalogy	Nicotine	Tobacco	Stimulant; insecticide
Caffeine[a]	Coffee, tea	Stimulant	Papaverine	Opium	Spasmolytic drug
Cocaine	Coca leaf	Local anaesthetic	Physostigmine	Calabar bean	Gastrointestinal and bladder stimulant
Codeine	Opium	Pain reliever			
Colchicine	Crocus	Plant genetics	Pilocarpine	Jaborandi	Diaphoretic (sweat producing)
Cusparine	Angustura bark	Stimulant	Quinine	Cinchona bark	Malaria fever
Emetine	Ipecac roots	Emetic; amoebic dysentery	Reserpine	Rauwolfia	Tranquilizer
Ephedrine	"Ma Huang"	Asthma	Scopolamine	Datura	Narcotic
Ergonovine	Ergot	Obstetrics; oxytocic	Sparteine	Broom	Cardiac treatment
Febrifugine	"Ch'ang Shan"	Anti-malarial	Strychnine	Strychnos	Pest exterminator
Mescaline	"Mescal buttons"	Hallucinatory principle	Tubocurarine	Chondrodendron	Nerve paralysis
			Yohimbine	Yohimbe bark	Aphrodisiac (sex stimulation)

[a] Sometimes classed as an alkaloid cf. (*1c*).

tropane, aconitine, senecio, veratrum, and yohimbine groups are encountered as esters of various organic acids of varying complexity. A few others occur as amides such as piperine and the ergot alkaloids.

The study of the chemistry of the alkaloids has been particularly attractive to chemists partly on account of their wide occurrence and diversity of physiological action on the animal organism and partly on account of the complex structural and synthetic problems involved in the elucidation of their structure. Many of these investigations have been classics in the realms of structure elucidation and synthesis. The occurrence and uses of some of the commoner alkaloids are shown in Table 1.

Isolation Methods

The presence of alkaloids in plants is first established by tests on extracts from the plant with various alkaloidal reagents (*3a*). The presence of a precipitate or turbidity with such common reagents as Mayer's (potassium mercuric iodide), Wagner's (iodine-potassium iodide), Dragendorff's (potassium bismuth iodide), Sonnenschein's (phosphomolybdic acid), and Scheibler's (phosphotungstic acid) indicates the presence of alkaloids.

"Mayer's reagent is most commonly used as it is generally the most sensitive. About 1 g of plant material is digested with 5–10 ml of dilute HCl and the filtrate tested with a few drops of the reagent. A creamy precipitate or turbidity generally indicates the presence of alkaloids."

The extraction of the total alkaloids from the plant material is generally accomplished either by extraction with acids or with organic solvents. Various modifications have been worked out empirically for the extraction of particular alkaloids. Solvent extraction is usually the more common procedure. The dried plant material is usually subjected to a preliminary extraction with light petroleum to remove plant oils. Most alkaloids and their salts are insoluble in petroleum. The alkaloid bases are then liberated from the salts present in the plant material by treatment with base (calcium hydroxide, ammonium hydroxide, or sodium carbonate) and then extracted with a suitable organic solvent such as chloroform, ether, benzene, ethanol, methanol, or methylene chloride. The alkaloids are then extracted with acid from the organic solvent or pasty residue that remains after removal of the solvent. The acid solution is made basic and again extracted with an organic solvent usually ether or chloroform to give a crude mixture of bases. Some alkaloid hydrochlorides are soluble in chloroform and this property can be used for purposes of separation (*5b*). A modification of the above process is the extraction of the plant material with an aqueous-organic solvent mixture and subsequent separation and drying of the organic layer. Non-basic alkaloids can usually be obtained after removal of any acid or alkaline constituents of the organic layer.

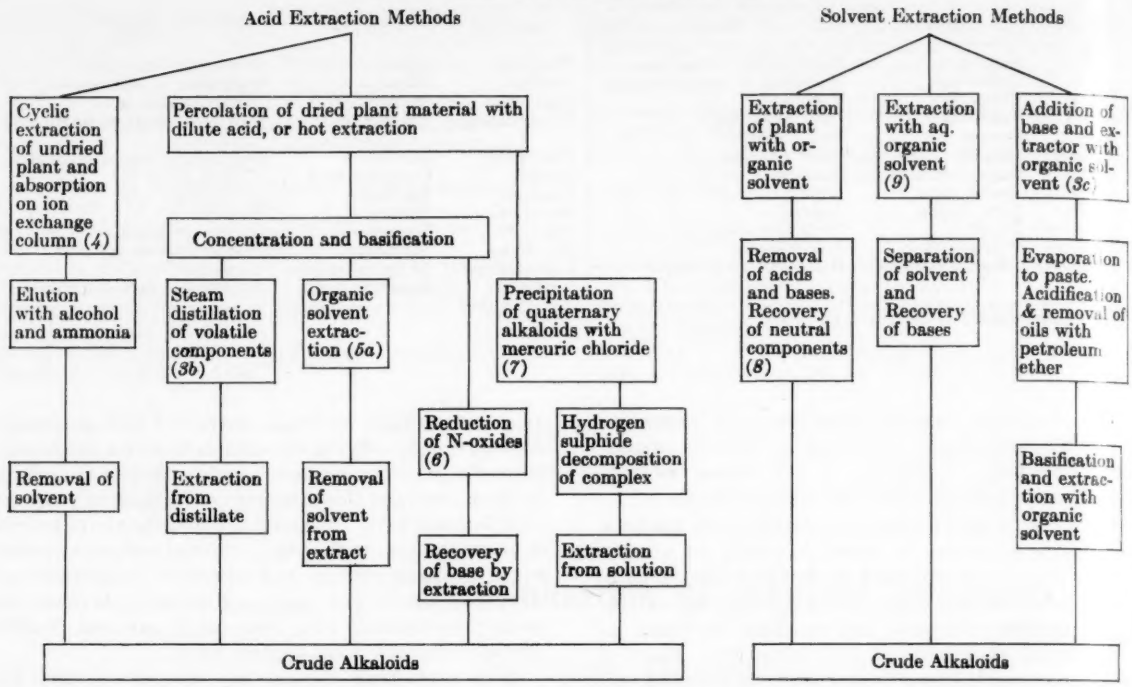
Acid extraction, though less frequently used, has been applied with success to the isolation of alkaloids from undried plant material in the field using ion exchange techniques. Alternatively the dried plant material is extracted with a dilute acid such as sulfuric or tartaric. Tartaric acid has the advantage of tending to give a purer product. Where there is danger of decomposition of the plant base, the extraction is done in the cold. The aqueous solution is basified and either extracted with an organic solvent or steam-distilled to remove volatile components. Quaternary alkaloids which are usually quite soluble in water are generally recovered by precipitation with mercuric chloride or Mayer's reagent and the resulting mercury complex decomposed with hydrogen sulfide. Some alkaloids which occur as N-oxides are quite soluble in water. They may be obtained by reduction with acid zinc dust followed by chloroform extraction. These methods are summarized in Table 2 with appropriate examples.

Separation and Purification Methods

In the early days of alkaloid chemistry the separation of mixtures of alkaloids often involved tedious fractional crystallizations or precipitations. Nevertheless, excellent separations were achieved. However the complexity of some alkaloid mixtures is such that for a time only the more abundant components could be examined. The advent of more elegant techniques of separation such as counter-current distribution, adsorption, and partition chromatography have made possible the study of many of the minor components (*10*). Ion exchange, though potentially a good method, has had little application in separation. These techniques are too well known to require elaboration. A summary of the main methods of separation with examples of their application is given in Table 3 and Figures 1 and 2.

Some criterion of the effectiveness of a separation is required. Paper chromatography and to a lesser ex-

Table 2. Examples of Alkaloid Isolation Methods


Acid Extraction Methods
Cyclic extraction of undried plant and absorption on ion exchange column (4)
Percolation of dried plant material with dilute acid, or hot extraction
Concentration and basification
Elution with alcohol and ammonia
Steam distillation of volatile components (3b)
Organic solvent extraction (5a)
Precipitation of quaternary alkaloids with mercuric chloride (7)
Reduction of N-oxides (6)
Hydrogen sulphide decomposition of complex
Removal of solvent
Extraction from distillate
Removal of solvent from extract
Recovery of base by extraction
Extraction from solution
Crude Alkaloids
Solvent Extraction Methods
Extraction of plant with organic solvent
Extraction with aq. organic solvent (9)
Addition of base and extractor with organic solvent (3c)
Removal of acids and bases. Recovery of neutral components (8)
Separation of solvent and Recovery of bases
Evaporation to paste. Acidification & removal of oils with petroleum ether
Basification and extraction with organic solvent
Crude Alkaloids

tent paper electrophoresis have been useful in this connection (Table 3, Fig. 3).

The individual alkaloid is characterized by constancy of its melting point, boiling point, optical rotation, ultraviolet spectra, infrared spectra, and any other suitable physical properties, and also by the preparation and characterization of derivatives and salts. Often the purification of an alkaloid through one of its salts is more convenient; a useful test for homogeneity is the inter-convertability of the alkaloid and its salts.

Quantitative methods of estimation of alkaloids which are generally either colorimetric, volumetric, or gravimetric depend largely on the types of functional groups present (*3d*).

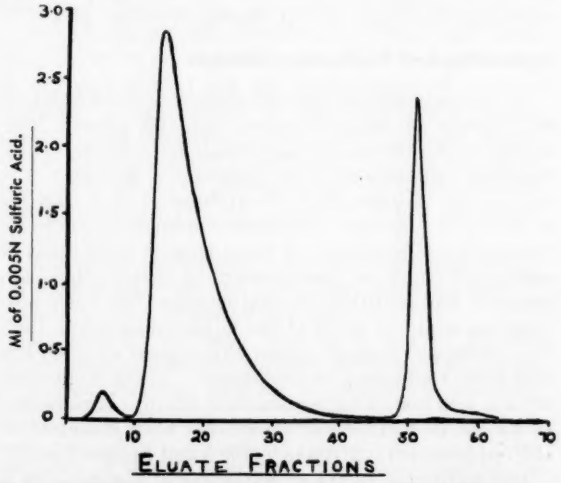


Figure 1. Partition chromatographic separation of pomegranate root bark alkaloids (by permission from the *J. Pharm. and Pharmacol.*) (*14*).

Structural Investigation by Physical Methods

Physical methods are becoming increasingly important in the structural elucidation of chemical compounds. A few examples of each method must suffice to illustrate the approach. It should also be emphasized that physical and chemical methods go hand in hand in structural investigation.

Ultraviolet Spectra

UV spectra have provided the keys to the solution of many problems in alkaloid chemistry. UV spectra may be useful in pointing to the type of structure likely to be found. Broadly speaking the spectra of alkaloids may be divided into three main classes (*26*).

No UV absorption in the range 200–1000 mμ. Examples are the saturated ring systems such as the pyrrolidine and piperidine alkaloids.

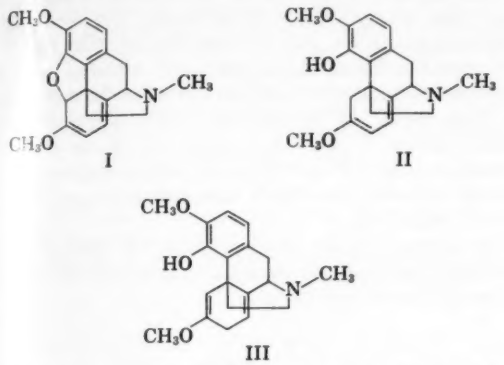
Simple aromatic chromophoric systems such as substituted benzene or pyridine with medium intensity absorption at relatively short wavelengths (230–300 mμ).

Alkaloids with complex chromophores, either aromatic nuclei in conjugation with other chromophores or fused aromatic systems.

Examples of the use of spectral methods in structure determination are seen with the alkaloids sempervirine (*27*), strychnine (*28*), and emetine (*29*).

The use of UV spectra in the assignment of structures is illustrated by the following example from the morphine series. The structure of the two dihydrothebaines was corrected by the use of UV spectra (*30*). The structure of the lithium aluminum hydride reduction product was shown to be II since the extinction values indicated a conjugated system. The structure of the sodium and ethanol reduction product was shown to be III since the extinction value showed a marked

lowering indicating the absence of a conjugated double bond system.



I. Thebaine
ϵ = 6500
λ = 283 mμ

II. $LiAlH_4$ product
ϵ = 11,000
λ = 284 mμ

III. Na/EtOH product
ϵ = 2000
λ = 282 mμ

The UV fluorescence spectra of some alkaloids have also been determined (*31*).

Infrared Spectra

Infrared spectra have been extensively used in the elucidation of the structures of organic molecules (*32, 33, 34*).

Some of the commoner functions found in alkaloids and their characteristic infrared absorption frequencies are shown in Table 4. The infrared spectra of alkaloids have been used for comparative purposes especially in the fields of drugs and narcotics (*35*), and also in following the course of synthetic and degradative experiments.

Thus the infrared spectra were used to reformulate the course of the synthesis of N-methylisomorphinane, IV. One of the intermediates in the synthesis was the postulated nitrile, V. This was shown to be incorrect as the infrared spectrum showed no nitrile bands at 2240 cm^{-1}, but showed bands at 3400 cm^{-1}, (secondary amine), 1664 cm^{-1} (cyclic amide), 1676 cm^{-1}, and 1692 cm^{-1} (cyclic conjugated carbonyl). The latter observations could be reconciled by a structure VI for the intermediate (*36*).

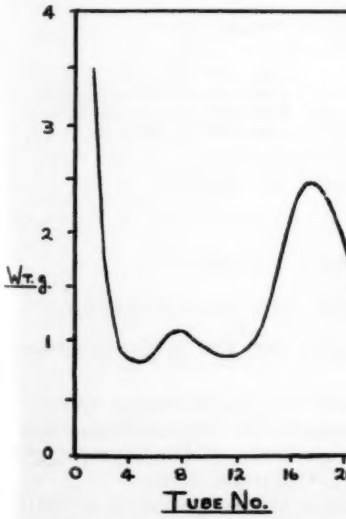
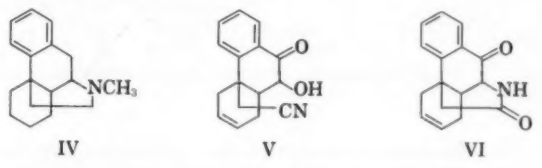


Figure 2. Twenty-four-tube counter-current distribution of veratrum alkaloids (by permission from *Anal. Chem.*) (*15*).

Table 3. Alkaloid Separation Methods

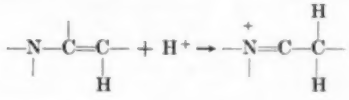
Method	Example of application	Reference	General reference
Fractional crystallisation	Quinine alkaloids	(*11*)	..
Fractional distillation	Hemlock alkaloids	*3(e)*	..
Separation by reaction	Veratrum alkaloids by acetylation	*12*	..
Adsorption chromatography	Senecio alkaloids	*13*	*19, 20*
Partition chromatography	Pomegranate root bark alkaloids	*14* (Fig. 1)	*19*
Counter-current distribution	Veratrum alkaloids	*15* (Fig. 2)	*21(a, b)*
Ion exchange	Yohimbine alkaloids	*16*	*22*
Paper chromatography	Curare alkaloids	*17* (Fig. 3)	*19, 25*
Paper electrophoresis	Strychnos alkaloids	*18*	*23, 24, 25*

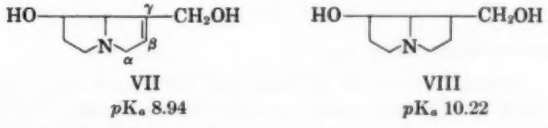


IV V VI

Basic Strengths and Polarographic Measurements

The determination of *p*K values has become increasingly important in structure determination and particularly in the elucidation of structural details. An example of this application is in the placing of the double bond in the structure of retronecine, VII, the alkanolamine hydrolytic cleavage product of the alkaloid monocrotaline (*41a*). The α-β or β-γ positioning of the double bond relative to the nitrogen atom was correctly postulated on the basis of *p*K measurements and subsequently confirmed by other methods. Retronecine is a weaker base than the corresponding saturated amine platynecine, VIII. This is compatible with a β-γ unsaturation whereas an α-β type of unsaturation would lead to an increase in basic strength due to the facile transformation:





VII
*p*K$_a$ 8.94

VIII
*p*K$_a$ 10.22

The application of *p*K values to the steric arrangement in some terpenoid alkaloids has been discussed (*42*).

The presence of a tropolone ring in colchicine was postulated on the basis of the similarities in the polarograms of colchicine and γ-thujaplicin (*43*).

X-Ray Crystallography

The application of X-ray crystallographic methods to the complex three-dimensional structures often encountered in alkaloid studies has been very rewarding

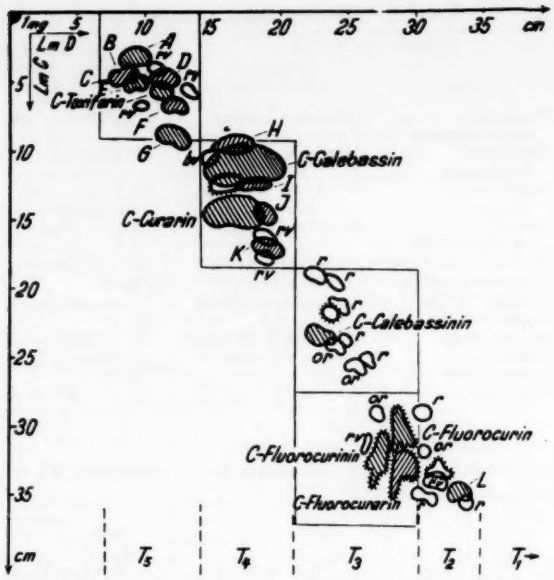
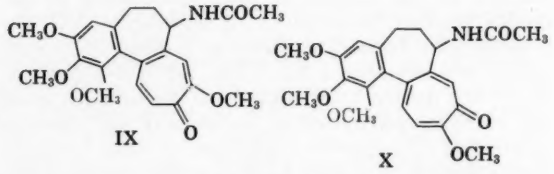


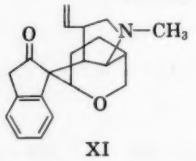
Figure 3. Paper chromatogram of curare alkaloids (from *Helv. Chim. Acta.*) (17).

(*41b*). Classical examples of the application are the studies of the alkaloids strychnine and colchicine. Thus the X-ray spectral method made it possible to distinguish between the structures IX and X for the alkaloid colchicine and showed that the structure X was the correct one.



IX X

Recently the structure of the complex alkaloid gelsemine, XI, has been independently postulated by both chemical and X-ray methods (*44*).



XI

Rotational Evidence

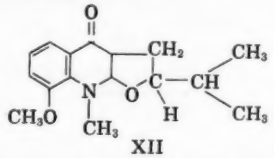
Optical rotational evidence has been used in a few cases to determine stereochemical configurations. Thus rotational evidence was used to establish stereochemical correlations between yohimbine and known steroid structures (*45*), and the absolute configuration of emetine has been deduced from optical rotational differences (*46*).

Optical rotatory dispersion has had limited application in the field of alkaloids, largely due to lack of suitable instruments, though some correlations between the diterpenoid alkaloids and the diterpenes have been made (*47*), and recently the absolute configuration of emetine has been independently determined with the aid of optical rotatory dispersion curves (*48*).

Nuclear Magnetic Resonance Spectra

The increasing interest in NMR spectra lies in the fact that many details of structure can be decided unambiguously by this method though this may not be possible using ultraviolet or infrared spectra. Also simple model compounds can be utilized to obtain a "fingerprint" of the portion of the spectrum under consideration. This is analogous to the use of model compounds in UV and IR work but in some cases the model suitable for NMR comparison may be more readily available.

An example of the application of the method in the complete proof of the structure of the alkaloid Lunacrine, XII, is outlined below.



XII

The structure was elucidated by a detailed analysis of seven well defined groups of lines in the NMR spectrum which were assigned as follows (*49*): (a) the hydrogen atom at position 5 of the quinolone system; (b) the aromatic hydrogen atoms at 6 and 7; (c) the α-hydrogen atom of the dihydrofurano ring; (d) the methoxyl- and N-methyl-hydrogen atoms; (e) the β-hydrogen atoms of the dihydrofurano ring; (f) the tertiary hydrogen atom of the isopropyl group; and (g) the C-methyl-hydrogen atoms.

Table 4. Some Infrared Absorption Characteristics of Alkaloids

Group	Infrared absorption cm^{-1} Intensity: S = Strong, M = Medium, W = Weak	Reference
—OH⁻	3625–3540 (S) non-associated 3400–3200 (S) associated	*32, 37*
Phenolic acetate	1767–1764 (S)	*38*
Alcoholic acetate	1742–1735 (S)	
C=O	1850–1620 (S)	*37*
C=N—	1660–1480 (S)	*32*
C=C	1680–1620 (S-M)	*32*
	near 3030 (W-M-S) 1640–1600 (S) near 1500 (W-M-S)	*32, 37*
	1690–1600 (S)	*32*
	3480–3460 (S) indole 3480–3440 (S) 2° amines 3280–3200 (S) associated 3380–3205 (S) 2nd amine	*37* *39*
Ammonium	2440–2350 (W)	*40*
Immonium	2100–1980 (W)	
NH_2 + 2° Amine salt	1620–1560 (S-M) deformation mode	
Hydrochloride salts	3000–2500 (M-W) Series of bands	*32*

Other examples of the application of NMR spectra in structure determination are illustrated by studies on the alkaloids lycodine (*50a*) and gelsemine (*50b*).

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"The Case of the Missing Joules," the Chem-Gem necklace which appeared on page 354 of the July, 1960, issue, has been the subject of detective work by several readers. Dr. Albertine Krohn of Toledo University and Mr. Kenneth V. Fast of Webster Groves High School (Missouri) write to say that it previously appeared in *C. & E. News*, June 15, 1953. The source there quoted was the Boston College Chemical Bulletin.

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Growth and Observation of Spherulites in Polyethylene:

A high polymer demonstration

The occurrence of spherulites, roughly spherical partially-oriented aggregates of submicroscopic crystalline layers (*1*, *2*), is commonly observed in most crystalline high polymers. The characteristic maltese cross extinction pattern and the range of colors arising in the birefringence of spherulites observed in the microscope between crossed polarizers make their study esthetically rewarding as well as of scientific interest (*3*). The ringed spherulites observable in higher density polyethylene are particularly spectacular (*4*, *5*).

The growth and observation of spherulites in higher density polyethylene is a simple experiment which can be carried out with a minimum of equipment. The only major item required is a microscope capable of 100–500× magnification, preferably equipped with polarizers. The experiment is thus well-suited for stimulating a beginning interest in research in high polymers, for example at the high school level. On the other hand, the experiment can readily be extended in several ways, as by photographing the spherulites or studying the dependence of their size and structure on time and temperature during their preparation. These extensions provide ample stimulation to the imagination of the more advanced student.

The experiments described below were tested by one of us (K. R. v. d. W.) as a project for the Los Angeles Science County Fair in 1959. In addition to the demonstration of spherulite growth, novel and useful techniques for color photomicrography were devised, and the illustrations for this article were produced (Fig. 1 and Fig. 2).

Procedure

Take proper precautions throughout to avoid burns from hotplates, hot specimens, or hot liquids.

Equipment. Hotplate whose temperature can be adjusted between 150 and 200°C; microscope slides; forceps; small oven capable of controlled temperature between 110 and 125°C, or crystallization bath; metal vessel large enough to hold microscope slides; hotplate equipped with rheostat or autotransformer, or other means of heating to controlled temperatures between 110 and 125°C; glycerine or ethylene glycol; and thermometer.

Microscope. If the microscope is not equipped with polarizers, two pieces of "Polaroid" material may be substituted, one above the eyepiece and the other somewhere below the specimen. Eyepiece scale (optional); microscope camera (optional).

Sample. Obtain a sample of higher density polyethylene. This material can be distinguished from low density polyethylene by its greater stiffness and resistance to deformation in boiling water. One common use for the plastic, which should furnish suitable samples, is sterilizable polyethylene baby bottles.

Preparation of Films

Adjust the temperature of the hotplate until it will melt the polyethylene readily (about 150°C) but will not degrade it, as evidenced by yellowing or bubbling (about 190°C).

Place several clean microscope slides on the hotplate. Allow about 1 in. of the end of each slide to extend over the edge of the hotplate so it remains cool enough to handle.

Place a small piece of polyethylene (about $^1/_{16}$ in. on a side) on all but one of the slides.

Using the extra slide, press the polyethylene out into as thin films as possible. Apply pressure with a wooden rod or other implement.

Scrape or smear the films of molten polyethylene still thinner with the end of the extra slide. Best results are obtained if the final films are about 0.001 in. thick or less.

Leave the slides on the hotplate with the polymer melted until they are to be crystallized. A waiting time of 10–15 min. is recommended to insure the growth of large spherulites.

Crystallization

The slides should now be removed from the hotplate and allowed to cool. As they cool below the crystalline melting point of the polymer (135°C), the films become somewhat translucent as crystallization takes place. (If the films look very translucent or opaque, they are probably too thick.) While cooling the slides in air on a cool surface such as a table top is satisfactory, the use of a crystallization bath or oven is recommended.

If a crystallization bath or oven is used, locate it near the hotplate and transfer the slides *quickly* to it so that they do not cool down below the temperature of the oven or bath.

Prepare the crystallization bath, if used, as follows: Heat glycerine or ethylene glycol in a metal (not glass) vessel to 110–25°C (see Control of Ring Spacing). Adjust the rheostat or autotransformer so that the selected temperature is maintained. Use forceps to transfer the slides quickly from the hotplate to this vessel. Leave the slides in the bath until crystalliza-

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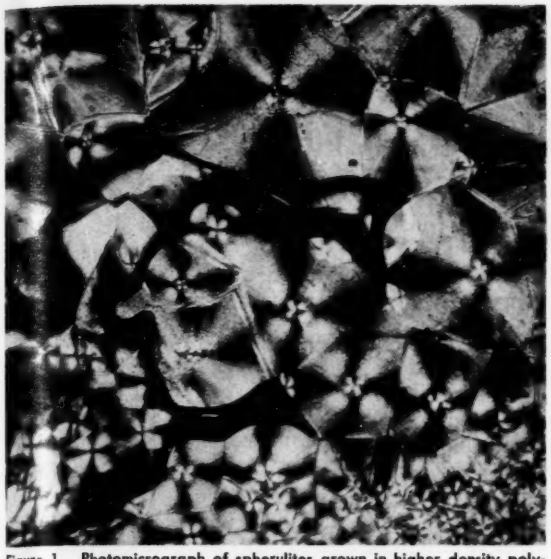

Figure 1. Photomicrograph of spherulites grown in higher density polyethylene. Crossed polarizers, magnification 100×.

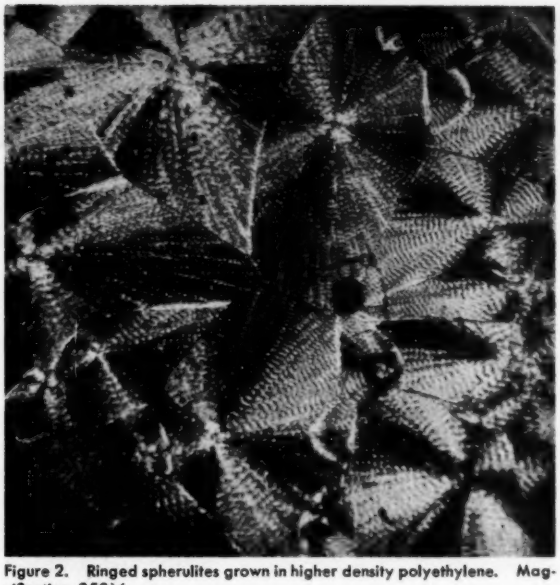

Figure 2. Ringed spherulites grown in higher density polyethylene. Magnification, 250×.

tion has taken place, as evidenced by the translucency of the polymer film. After the polymer has crystallized, remove the slides from the bath with forceps and allow them to cool to room temperature. Wash them with water and dry them.

Control of Spherulite Size. The size of the spherulites is controlled by varying the length of time the slides remain on the hotplate before crystallization. Longer times, beyond the 1–2 min. minimum required to anneal out the effects of smearing the film, give larger spherulites. The maximum time, which may be about 1 hr., is set by the appearance of signs of degradation, and thus depends on the temperature of the hotplate.

The growth of spherulites in polyethylene under these conditions is initiated from microscopic or submicroscopic particles called nuclei or "seeds" (*6*). Growth normally continues during crystallization until the boundaries of adjacent spherulites come together, the whole sample being filled with spherulitic material. The size of the spherulites thus depends on the number of nuclei from which growth begins. It is also known that nuclei are progressively destroyed as the polymer is kept at melt temperatures. Thus longer times in the melt and higher melt temperatures lead to fewer nuclei and larger spherulites.

Control of Ring Spacing. The spacing of the rings is controlled by allowing the slides to crystallize at different rates, the rate of crystallization being controlled in turn by the temperature of the crystallization bath. At temperatures considerably below the crystalline melting point (110–15°C), crystallization is complete within a few seconds and the spacing of the rings is quite narrow. At higher temperatures (120–25°C) crystallization takes considerably longer and the spacing is wider.

Observation

Observe the spherulites in the microscope at magnifications between 100 and 500. They must be observed between crossed polarizers, i.e., polarizers rotated so that the field is dark when no specimen is in place.

If an eyepiece scale is available, measure the diameters of several spherulites on one slide. Average the spherulite diameter and plot it on graph paper against the time the slide was held on the hotplate. (A good correlation will be obtained only for those slides for which hotplate temperature and cooling conditions were constant.) Measure the spacing of the rings on those slides where crystallization bath temperature was varied, and plot the spacing against this temperature.

If the microscope has a camera attachment, or if there is a camera with a ground glass focusing back available, take photographs of the preparations. The photographs in Figure 1 and Figure 2 were made with a Speed Graphic camera. The lens was removed and the bellows was placed over the microscope eyepiece, the image being focused on the ground glass back. The focal plane shutter was used. For black and white photographs Kodak Tri-X film was used, whereas for color photographs, Super Anscochrome Tungsten, rated at ASA 100, was utilized.

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Physical Chemists in Berlin, 1919–1933

In the period from 1919 to 1933, many of the outstanding physical chemists of Germany were centered in Berlin. These included Nernst, Haber, Bodenstein, Volmer, and Bonhoeffer. At the same time many renowned scientists in allied fields were also present. Therefore a center of physical chemistry developed which was unequalled anywhere in the world at that time. In allied fields, Max Planck was working on thermodynamics, von Laue on crystal interference, and Schrödinger and London on development and application of wave mechanics. Simon and Meissner were working on low temperatures. For spectroscopy there was Paschen at the Physicalisch-Technicallische-Reichsanstalt and also Warburg who made the experimental foundation of photochemistry. Still other outstanding groups were present; for example, Otto Hahn and his co-workers on radiochemistry and G. Hertz who worked on the separation of isotopes by gaseous diffusion. The factors which brought about and made such a possible concentration of scientific talent were singular.

It would almost be presumptuous of me to try to review the great era of physical chemistry which occurred in Berlin after World War I and extended until 1933. However, I may speak of famous men whose names can never be forgotten in the history of natural science and make comments regarding their personality and work because I am one of the few who can speak from his own personal experience. I must be allowed, however, to make two limitations: first, I shall speak in detail of only those scientists who were connected with physical chemistry and whose work has been important in this field. Secondly, I would prefer to speak more about the scientists who are no longer among us because their places in history are rather well established.

Scientific Atmosphere in Berlin

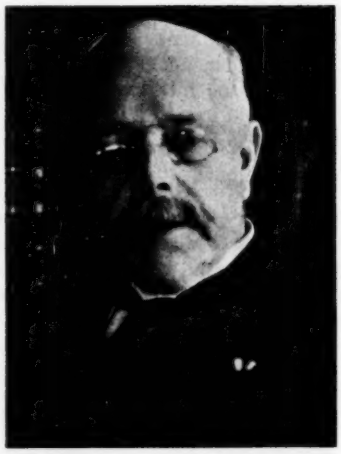
Berlin in the year 1919 was the capital of a country which had just lost World War I, but even in those times of revolution, inflation, and uncertainty in politics, intellectual life and scientific culture started to develop. The technical and exact natural sciences and even the scientists themselves were held in high esteem. There was a very well-educated and cultured class which was not too large, but was able to produce scientists who became world-famed. At the same time scientists from other countries who could speak German and had German cultural ties were accepted in Berlin; thus there was an intellectual exchange with the whole world. There still exist friendships and relationships begun during this time among scientists all over the world.

Since most of the institutions were government-sponsored, it was very important to have high government officials who were broad-minded and intelligent people. The funds for the institutions were adequate, although not excessive, but the most important thing was the scientific atmosphere and the scientific enthusiasm which was unique during this period. It was very important for the development of physical chemistry in Berlin of those days that exceptionally good scientists headed the institutes of physical chemistry of the University, the Polytechnic Institute in Berlin-Charlottenburg, the Kaiser Wilhelm Gesellschaft (now the Max Planck Society), and the Physikalisch-Technische Reichsanstalt (equivalent to the Bureau of Standards in the United States). W. Nernst held the chair for physical chemistry at the University from 1905 till 1922 when he became President of the Physikalisch-Technische Reichsanstalt. He was succeeded in the chair of physical chemistry by Max Bodenstein. The institute for physical chemistry of the Kaiser Wilhelm Gesellschaft was headed by Fritz Haber, and the institute of physical chemistry of the Polytechnic Institute was headed by Max Volmer, a specialist on the kinetics of phase formation. In addition, G. Hertz was head of the experimental physics at the Polytechnic Institute, and in these years he performed his classic work in the field of isotope separation, which was actually a development in physical chemistry. The presidents of the Physikalisch-Technische Reichsanstalt before and after Nernst were O. Warburg and Paschen. Noddack, the discoverer of rhenium, with his low temperature laboratory worked in fields which were allied to physical chemistry at the Physikalisch-Technische Reichsanstalt. In the old Nernst institute of the University there was a lucky combination of the Nernst tradition, represented especially by F. Simon, with the experimental skill of the new director Max Bodenstein in the field of reaction kinetics. The atmosphere at Kaiser Wilhelm Gesellschaft in general and the institute for physical chemistry in particular was certainly novel. The possibilities of working in a well equipped institution, under very favorable conditions, and devoting full time to research were very unusual in those days in Germany. In the interval after World War I till 1933 these men controlled almost all the physical chemistry in Berlin. They were Walter Nernst, Fritz Haber, and Max Bodenstein, and therefore I may be allowed to enlarge upon each of these three scientists.

Read by Gene G. Mannella as part of the Symposium on Inorganic Chemists in the Nuclear Age before the Division of History of Chemistry at the 134th Meeting of the American Chemical Society, Chicago, September, 1958.

Walter Nernst (1864–1941)

The education of young Nernst was the usual one of a young German physicist. Since his first scientific achievements were made under the guidance of the physicist Friedrich Kohlrausch in Werzburg and Boltzmann and Ettinghausen in Graz, the most important event for his future life was his decision to go to Wilhelm Ostwald in Leipzig in 1887 as an assistant. Even though he was much younger than the three dominating figures of Arrhenius, Ostwald, and van't Hoff, who at this time were in Leipzig, he soon developed as one of the founders of the new discipline, physical chemistry.



Fr. Walther Nernst.

In 1891 he became associate professor in Göttingen, in 1895, full professor and department head in Göttingen, and in 1905, professor of physical chemistry in Berlin. In 1922 Nernst became president of the Physikalisch-Technische Reichsanstalt, and in 1924 he returned to pure physics and became the professor of physics of the University of Berlin. So we may say that at the end of his career he turned back to pure physics, but his really important works were practically exclusively devoted to physical chemistry.

His works during his lifetime must be considered overwhelming and, therefore, I must confine myself only to the enduring highlights of his career. I shall draw from Max Bodenstein who wrote some very excellent articles on Nernst and his work. Even his first independent research became an important achievement for electrochemistry. From the assumption that a metal which is immersed in an electrolyte behaves like a reservoir of ions under a characteristic "electrolytic solvation pressure," it was possible to calculate the maximum electric work for this procedure and to bring this in line with the experiments. Along such lines he performed many investigations which are still fundamentals of electrochemistry.

The problem of chemical equilibrium was the second and perhaps even more important achievement of Nernst, and the research in this area led him to discover the third law of thermodynamics, which brought him immortality. The assumption that at the absolute zero the free energy and the heat of formation become identical together with a series of ingenious experiments and theoretical analyses led him to this eminent discovery. Since much needed data were not available, for example, the specific heats of solid substances and gases, he developed for this purpose the vacuum calorimeter and constructed a small hydrogen liquefier so that the desired data could be obtained down to a temperature from which it was possible to extrapolate safely to absolute zero. If anybody did not agree to call his "theorem" the third law of thermodynamics, but only a way of calculating chemical equilibrium from thermodynamic data, combined with much from quantum theory and quantum mechanics (the latter having in principle nothing to do with thermodynamics)—if anybody was bold enough to make such a remark, Nernst would visualize such a man as his very personal enemy. Still, as far as I know, no biography of Nernst has been written which measures up to the performance of such a unique man of genius. His textbook of physical chemistry was first edited in 1893 with many editions following. It was, in the German language, *the* textbook for physical chemistry. Only after 1925 other textbooks came into the foreground like those by A. Eucken and J. Eggert, both of whom were pupils of W. Nernst. The majority of his outstanding works were done before World War I, and with his return to pure physics, his productivity began to fade. His dominant influence in physical chemistry, however, was unchallenged, and it would have been hard for a scientist in Germany who was not accepted by Nernst to succeed.

Nernst was an unusually gifted personality. His combined imagination, objectivity, technical skill, and the theoretical mastery of his material were almost

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W. NERNST

Walter Nernst hatte eine Abneigung gegen die Einführung von neuen Einheiten. Als das "Hertz" als Einheit der Schwingung eingeführt wurde, erklärte er ungehalten: "Ich würde vorschlagen, eine Einheit für die Durchflussgeschwindigkeit von 1 Liter pro Sekunde zu wählen und sie ein 'Falstaff' zu nennen."

From "Chemiker-Anekdoten" (new edition entitled "Was nicht in den Annalen steht"), published by Verlag Chemie, Weinheim/Bergstrasse, Germany. (*See* page 466.) M

unparalleled even by the outstanding physical chemists in those days. In addition, if he liked, he could be a brilliant teacher or speaker and improvise speeches, but he had certain pecularities which will have to be mentioned. For example, in his lectures he related practically everything to his own work, or works of his pupils, so that a student who attended his lectures got the impression that most of physical chemistry and related fields were worked out by Nernst. I heard the following with my own ears:

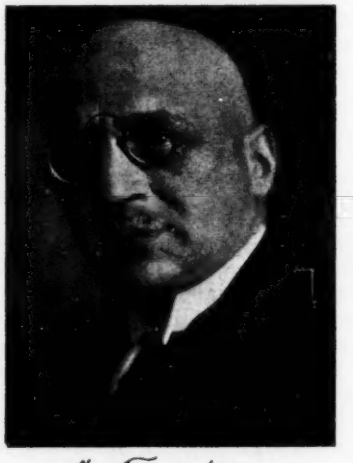
> The first law of thermodynamics is due to the experience in natural science that we cannot make energy or heat from nothing and that to a certain amount of heat a certain amount of energy is equivalent. The second law of thermodynamics is due to the investigation of a group of very eminent scientists who have shown to what extent under determined conditions heat can be transformed into work. And concerning the third law of thermodynamics—this I have just done myself alone.

But his eloquence and his mastery in discussion sometimes misled him to defend a standpoint which he himself did not accept. Sometimes it seemed that he only enjoyed demonstrating his superior dialectic.

In the physics colloquium in Berlin which was chaired by Max von Laue there were, among other outstanding participants, Einstein and Planck. Nernst obviously had the correct feeling that, compared to the gigantic performances of Einstein and Planck, even his third law of thermodynamics was not entirely equal in importance and, true to his nature, he would not miss an opportunity to object when one of these two scientists made a statement, or to try to direct the discussion to a field in which he felt himself superior. He could do this with so much wit and charm that all, and even those involved, were very amused. Nernst was able to invent a story or innuendo on the spur of the moment and if there was a meeting with scientists who knew him, or with his pupils, at which he did not tell a story or make witty remarks they would be a little disappointed. Because he passed away during the war, there is no adequate biography of Nernst and there is danger that all these anecdotes may become forgotton. It would be a pity if they were lost. Despite all his stories and jokes at the expense of other people, Nernst was a typical "Geheimrat," and I wonder if in his later years, he was close to even one of his pupils. If you met one of the former pupils of Nernst it did not take long before he began to speak of the unique times he had had under Nernst, who inspired him; but his admiration was always superior to his devotion.

Fritz Haber (1868–1934)

At the same time another of the really great physical chemists was in Berlin. It was of interest for me to learn from Wilstätter's autobiography in which he dedicated a chapter to his old friend Haber, that during his studies, and during the time he worked toward his Ph.D. as an organic chemist, and even in the years afterwards when he was assistant professor, Haber was just a young man with unusual energy and activity. No one who knew Haber at this time would have thought that he would develop into such an outstanding personality. Haber's friend Wilstätter called this period "seven years of detours and errors," and he thought that the reason for this was that Haber was a man who could not fit into poor surroundings. When he came to Karlsruhe where he spent seventeen years of his life (obviously too many), he at least had the influence of Bunte and Engler to whom he was deeply devoted the rest of his life. Haber succeeded in doing a very unusual thing in Karlsruhe. From his base in organic chemistry, he taught himself physical chemistry and performed highly-rated research work in electrochemistry. The greatest moment in his life came when he succeeded in performing his ammonia synthesis from nitrogen and hydrogen in the years before World War I. At this time Haber was a highly esteemed scientist to whom the directorship of the institute of physical chemistry of the Kaiser Wilhelm Gesellschaft was given. Now he became a man of world-wide prestige and after the war was awarded the Nobel Prize for chemistry. In World War I the ammonia synthesis was an important factor because by this means it was possible to compensate for the loss of the nitrates imported from Chile. The nitrates produced from the ammonia by the Haber-Bosch method were not only important for the warfare, but in addition they were needed as fixed nitrogen for fertilizers. This fact saved many millions of people of Germany from near-starvation during World War I. Haber liked to assume this use even more important than the fixed nitrogen for warfare. Haber also played an important role in other fields of the war economy and in the warfare with poisonous gases. He considered



Dr. Fritz Haber

himself to be a good German and the defeat affected him very deeply. Above his desk in his home in Berlin hung the picture of Kaiser Wilhelm the Second, with a personal signature of the Emperor; it remained there until 1933, when he left Germany for England.

After World War I he started another huge endeavor—trying to recover gold from sea water since Germany had to pay reparation in foreign currency and gold, which was obviously impossible. This work was not successful because the assay of gold of the waters of the seas as reported in the literature was much too high. Ironically, Haber succeeded in developing a method which would have economically produced gold from the waters of the seas if the data in the literature had been correct. This type of enormous project was probably more in line with his energy and talent for organization than pure research under limited subsidy.

It was, therefore, very fortunate that this technologically-great deed gave him real and ideal backing to develop his institute and organize it in such a way that it became, without a doubt, the leading institution for physical chemistry in those days. Scientists, young and old, and many guests were in contact with Haber's institute. To mention them and to weigh their merits would be difficult and go far beyond the scope of this paper.

The publications of Haber's institute which appeared in various periodicals were edited in book form. This impressive volume contained progress in almost all fields of physical chemistry. Haber, by his personality, gave tone to the institute. He was wise enough to know that one has to give to the group leaders and also to keen young members of the institute far-reaching scientific freedom to develop an atmosphere of free scientific thinking and enterprise. In later years he made trips away from the institute for weeks or months; when he came back he would call all his pupils and ask them "While I was away who did some nice work that an old man would enjoy?"

In Haber's institute there were different departments. Freundlich headed the department for colloid chemistry, Ladenburg, spectroscopy, Polanyi, kinetics, and to a certain extent all departments did pioneer work in their field. Kallmann was the right hand of Haber in the administration of the institute. His research work included mass spectroscopy and high voltage particle acceleration which tended toward nuclear physics. K. F. Bonhoeffer joined the institute in 1922 after working with Nernst for his Ph.D. in physical chemistry.

Up to this time the problems of thermodynamics had been in the foreground not only in teaching but also in research. But to far-seeing people it became obvious that the problems of pure thermodynamics could not answer many important and interesting questions. It is obviously one of the most noble duties of physical chemistry to make use of the discoveries in pure physics for solving problems of chemistry. This field, on the boundary line between physics and chemistry, which was developed by Ostwald and his contemporaries, and which is always in a state of development, has attracted outstanding scientists, sometimes from the field of physics and sometimes from chemistry. It was obvious after World War I that the time was ripe for some change in attitudes in applying the approaches of new fields to physical chemistry. Band spectroscopy and quantum mechanics became attractive for solving chemical problems in general, and photochemistry and reaction kinetics, to some problems in particular. The combination of nuclear physics and chemistry opened up new directions of investigation. Spectroscopy and quantum mechanics were developed to a large extent in Germany during these times.

Bonhoeffer took full advantage of this situation and as a young scientist produced much outstanding work in a few years on different lines at the institute. I would like just to mention his work on hydrogen atoms, predissociation, parahydrogen, OH radicals, and the paper with Haber in which spectroscopy was used for problems of combustion. Bonhoeffer was perhaps the pupil whom Haber liked most, and Bonhoeffer could not have shown greater gratitude to Haber than by his last efforts to re-establish in Germany the new institute of physical chemistry of the Max Planck Society at Göttingen. In West Germany this is the successor of Haber's institute in Berlin-Dahlem. Bonhoeffer developed this institute in Haber's spirit and brought it to international recognition in a few years. Each young man who had the opportunity of working close by with Haber had, in addition to his scientific gains in knowledge, the opportunity to learn things which frequently became increasingly important to him in a more general way. From all his advice I have just two comments that I would like to recall. Once Haber said:

> It is too bad there are so many people who think only a few days on what problem they will work, then they will work hard for two years and write the whole thing together in one month, instead of spending about equal amounts of effort on these three points.
>
> It is perhaps easier and certainly much more gratifying to work in fields which are entirely novel, if a man can do so. The difficulty of reading through and evaluating the enormous amount of work of others in an older field may stifle any creative productivity.

No one who had ever been in contact with Haber would ever forget his personality. I would like to mention that one of his long-time assistants became so influenced by thoughts and ways of Haber that he not only started to speak and act like Haber but that his handwriting became so similar that it could hardly be distinguished from Haber's. The end of Haber's institute in 1933 was a great loss for physical chemistry and an almost unparalleled shame in the history of natural sciences. It was not only an unparalleled ingratitude with respect to the unique merits of Haber, but there was also a full misunderstanding of the singularity of this institute and the impossibility to regenerate it by will alone.

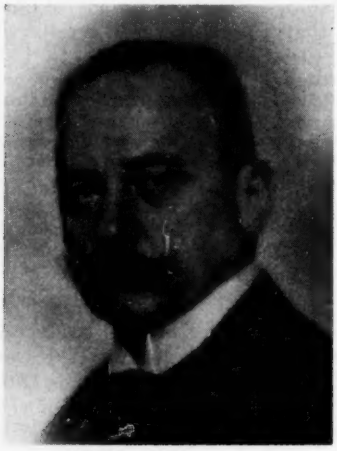
After the war it was one of the duties of the Kaiser Wilhelm Institute (now Max Planck Society) to honor the memory of Haber. I think his former pupil, J. Jaenicke, is now writing Haber's biography.

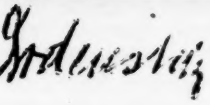
Max Bodenstein (1871–1942)

The third outstanding physical chemist in Berlin at this time was Bodenstein. Bodenstein did not have the brilliance of Nernst, and I think to a certain extent he looked up to Haber. In these days theoretical physics was most highly regarded in Germany, especially in Berlin, perhaps because of the outstanding theoretists like Einstein, Planck, Schrödinger, and von Laue. I think Bodenstein was himself a little under the influence of this almost overemphasis on theory. Even a young scientist who performed practically nothing but was very good in theory was highly esteemed by Bodenstein, but at the same time he himself was one of the most outstanding experimenters, and his skill is still admired. It is hard to understand how Bodenstein was able to study reaction kinetics with almost absolutely pure gases fifty years ago. In those times one did not have dependable high vacuum pumps; liquid air and dry-ice were seldom available. Stopcock grease which had almost no vapor pressure did not exist, and the quality of the glassware was poor compared with the standards of today. Despite all these handicaps

Bodenstein and his pupils performed outstanding work. The reactions which he investigated, like the formation and decomposition of hydrogen iodide, the formation of hydrogen bromide, and in later years the formation of hydrogen chloride and the formation and decomposition of phosgene, were studied in such manner that the results stand today.

He had many pupils who became famous scientists. I would just like to mention S. C. Lind, the dean of radiation chemistry, and G. Kistakowsky at Harvard, who are both very well known. I also appreciate the





good fortune of having been accepted as a Ph.D. candidate by Bodenstein, who gave me the basis for my further experimentation. As time goes on and as kinetics becomes more and more important, I hear people complain sometimes that Bodenstein is one of those who should have received a Nobel Prize.

I would like to mention that Nernst, Haber, Bodenstein, and Bonhoeffer all came from very wealthy families, like the majority of the scientists in physics and chemistry in those days in Germany, especially in Berlin. In those days a professor who was world-famous had an outstanding position in Berlin. He ranked high in society and money was no problem to him. In his wealthiest years Haber was considered to be a multimillionaire.

For an outstanding professor, especially in Berlin, life was full of work which could almost kill a man without exceptional strength. People always expected an outstanding scientific performance from him; he was a member of the Academy of Science in Berlin, had to give lectures, make up examinations, do his share of committee work, and write textbooks. When I was a young student in Berlin I was shocked, watching such a performance.

In those times, even when Berlin was the center of gravity for physical chemistry, the rest of Germany was rich in outstanding scientists and institutes. In Hamburg, Otto Stern developed molecular ray research techniques to a degree of perfection which has not been surpassed today. This was in a city where the University in general and research in particular were not accepted by a large part of the influential people. The institute in Leipzig founded by Ostwald, followed by Leblanc and then by Bonhoeffer, was second only to Berlin and at about the same high level as the Institute in Göttingen. There, following Nernst, Tammann did his pioneer work on metallurgy and was followed by A. Euchen. Euchen was one of the most outstanding pupils of Nernst.

Today's Perspective

Today it is hard to understand that in the early thirties some prominent scientists thought that physical chemistry had reached a certain endpoint, that the fields which belong to physical chemistry had been developed in their main lines and there were only small remainders. It looked as if it would soon be necessary to look only for complicated unsolved problems. The Raman effect, parahydrogen, and isotope work more or less appeared to be very interesting residues. The field of radioactivity was not acknowledged a discipline belonging to physical chemistry at that time. The work of Otto Hahn and his group in Berlin-Dahlem, of G. von Hevesey, and F. Paneth had not been in the usual trend of research, and only a few may have surmised that this was pioneer work in preparation for future developments. The stagnation in physical chemistry was only temporary. In a short time discoveries like the artificial splitting of atoms, the neutron, deuterium, artificial radioactivity, practical methods to separate isotopes, and the application of electronics for experimentation in physical chemistry were made. These gave a feeling that in the near future things would be in a realm of possibility not previously imagined. Indeed in the early thirties a new wave of problems came from physics to physical chemistry with the only difference being (as seen from the German point of view) that in all these discoveries and developments Germany was participating to only a minor extent. This may have been just a little fluctuation. But I do not think that it would be correct to explain this fact in this way. I had the opportunity in the years 1933–34 to work in Rutherford's Institute, at Cambridge, England, and when I looked at the way people performed their experiments and the way they overcame experimental difficulties, I got the impression that there was nothing superior in Germany and that the discovery of deuterium by Urey did not just come about by good luck. Perhaps people in Germany had become a little too self-complacent and underestimated the ability of foreign countries. This would certainly have been overcome and Germany would have regained her role if the "Third Reich" had not created a discontinuity in scientific development which has not been overcome even today. I think it is a real lesson for other countries to realize this and not forget it.

CHEMIKER ANEKDOTEN. Nernst had a phobia against dragging in new units. When the hertz was introduced as a unit of frequency, he boldly proposed, "Let's have a unit for rate of throughput, 1 liter per second, and let's call it 1 falstaff." (*See* page 463.)

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The Role of Imagination in Science

Van't Hoff's inaugural address

The sciences are practical in the profoundest sense of the word. In order to reach a certain goal, it is sometimes easier to go around the difficulties in the way instead of fighting them; the former is often possible when the latter exceeds our strength. Yet we would be forced to attempt the direct assault if no relation existed between what is and what is to come.

This relationship in fact exists; in its totality we call it the relation between cause and effect. Science sets as its task the elucidation in every detail of this relationship.

For this reason I called science practical in the profoundest sense of that word; it is the great aid by which our surroundings become subject to our will.

In the light of what has been said, our subject can be stated more accurately as "the role of the imagination in elucidating the relation between cause and effect."

We shall designate by "Imagination" (Phantasie), the capacity to visualize a particular thing so clearly, that all its properties can be recognized with the same certainty as if the object were directly observed. It is now only necessary to describe the mechanism by which the relation between cause and effect may be studied, and to find the place where the capacity we have described plays a part. This mechanism is a very simple one. It consists of two parts:

(1) By observation, the attempt is made to attain exact knowledge irrespective of our particular environment.
(2) The causal relationship underlying the observations is sought.

While observation as such, the conscious accounting of the impressions impinging on our sensory tools, requires only practice and the capacity to concentrate one's attention, higher demands are to be met by that which lends observation its high value: (*a*) in the choice of time or of the object of observation, (*b*) in the planned modification of the observed, (*c*) in the finding of those aids which simplify the observations or even are necessary in order to make the observation possible.

Translator's Introduction

As the interest in the subject of creativity[1] and of the creative process in the sciences increases, it is well to turn first to the scientists themselves to determine their own views on the process by which science makes its strides into the unknown. A major contribution to the subject was made by Jacobus Henricus van't Hoff (1852–1911) in his Inaugural Speech as Professor of Chemistry at the University of Amsterdam.

Van't Hoff's 11-page pamphlet "Proposal for the Extension of currently employed Structural Formulas into Space, and a Comment regarding the Relation between Optical Rotatory Power and Chemical Constitution" (1874) was expanded the following year into "La Chimie dans L'Espace." This work was translated into German by F. Hermann, and carried a preface by Johannes Wislicenus, whose own work was the direct cause of van't Hoff's geometrical proposals:

> "Gentlemen" said van't Hoff at a later date, "I will give you a recipe for making discoveries. In connection with what has just been said about libraries, I would like to remark that they have always had a deadening influence on my mind. While engaged in studying the Wislicenus article on the lactic acids in the Utrecht library, I interrupted my perusal half way in order to go for a walk. It was on this walk that through the influence of the fresh air the idea of the asymmetric carbon atom arose in me."[2]

Wislicenus' preface drew upon van't Hoff the fury of Hermann Kolbe, and the latter's attack made van't Hoff famous almost overnight:

> "I would have ignored this work (van't Hoff's *La Chimie dans L'Espace*)" wrote Kolbe, "as I have done many others, had not a significant chemist taken it under his protection and recommended it as a worthy achievement. A Dr. J. H. van't Hoff, employed at the School of Veterinary Medicine at Utrecht, finds, so it seems, exact chemical research not to his taste. He has thought it more convenient to mount Pegasus (borrowed, no doubt, from the Veterinary School) and to proclaim in his "La Chimie dans L'Espace" how on his daring flight to the chemical Parnassus the atoms appeared to be arranged in space.... To criticize this paper in any detail is impossible because the play of the imagination completely forsakes the solid ground of fact and is quite incomprehensible to the sober chemist."[3]

The attack by Kolbe on the use of the imagination in science led van't Hoff to choose that particular topic for his inaugural address. The translation is a slight condensation from the German version of E. Cohen.[4] It has been checked against the original published in Dutch.[5] In part it reports a rough statistical analysis of the lives of over two hundred famous scientists. Van't Hoff noted that creativity in science often resides in the same person as notable potentialities in the arts. Further, van't Hoff claimed to have found a significant proportion of eminent scientists who showed behavior close to mental illness. Calm and relaxed students do not, it seems, necessarily become the best scientists.

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[1] This is the second article in a series on creativity. The first article was August Kekulé's speech at the Berlin benzene celebration, translated in "August Kekulé and the Birth of the Structural Theory of Organic Chemistry in 1858," J. CHEM. EDUC., **35**, 21–23 (1958).

Supported by National Science Foundation Grant G4207.

[2] COHEN, E., "Jacobus Henricus van't Hoff," *Akademische Verlagsgesellschaft*, Leipzig, **1912**, p. 85.

[3] KOLBE, H., *J. prakt. Chem.*, (2), **15**, 473 (1877); A complete translation of the Kolbe tirade appeared in WHELAND, G. W., "Advanced Organic Chemistry," 2nd ed., John Wiley & Sons, Inc., **1949**, p. 132.

[4] COHEN, *op. cit.*, pp. 150–165.

[5] VAN'T HOFF, J. H., *"De Verbeeldingskracht in de Wetenschap,"* P. M. Bazendijk, Rotterdam, **1878**, pp. 4–24.

These are three antecedents in which quite different capacities play a role than trained sense organs and concentration.

Choice of time or of the object of observation: Some time ago the French astronomer Leverrier, shortly before his death, predicted the existence of a new planet in the vicinity of the sun. He appealed to several observatories, and these sought the planet at the moment when, located between the earth and the sun, it might become visible as a dark disc on the latter. These observations were not crowned with the desired results.

An American chose a different occasion; he had the idea that during a solar eclipse this planet should become visible in the same way as the moon is at night. In fact Vulcan was observed for the first time on this occasion.

For this so-called "hitting-on-the-idea" it is necessary to survey the possibilities in thought and to make a definite choice. In other words, it becomes necessary for imagination and judgment to work together. Of still greater significance than the choice of the object or the moment of observation is the *deliberate modification of the observed.* It is in this way that the possibility of choice is opened to us. In the study of fermentation, Tyndall sought to discover what would happen when the system is changed in such a way that the air in contact with the fermenting substance is freed from the small dust particles floating in it, particles that show their presence in a beam of light. These dust particles were removed with great ease by covering the inner walls of the box in which the experiment was performed with glycerin; after some time, even the smallest dust particles remained stuck on the walls, like flies on a tarred fence. Again, it was the imagination that made him hit on the idea.

Thirdly, we consider *the aids which simplify and often make possible an observation.* The direct observation of the retina through the pupil of the eye, although completely transparent, is impossible because the observer stands, so to speak, in his own light. If a flame is placed between the object of observation and the observing eye, the retina would indeed be illuminated, but it could not be observed. Helmholtz hit on the idea of placing a small mirror with a small opening between the eyes in such a way that light impinging obliquely enters the eye to be observed, while the opening in the mirror permits the eye to be observed. This cooperative work of imagination and judgment led to the discovery of the optical mirror.

So much for the first part of the mechanism. Its use leads to the exact knowledge of our environment; but this knowledge is of a complex whole, consisting of conglomerations of causes and effects.

Cause and Effect

It is now necessary to disentangle out of this chaos, piece by piece, the threads that bind each cause with the effect connected with it.

The manner by which this happens can be described by the following metaphor (J. S. Mill, "System of Logic"):

Several musicians, A, B, C, etc., are playing different instruments at the same time behind a curtain. We think of the musicians as an interconnected whole of causes; the concert they play is the conglomeration of effects. To ascertain the relation between each particular cause and its effect requires the knowledge of the instruments played by each musician. The simplest procedure would certainly be to ask all the musicians except one, for instance A, not to play for a moment. Sometimes this is not possible, and only the other musicians together can be made to play a little louder or somewhat less loud. In other cases we are forced to be satisfied with letting A stop playing or to let him vary his playing also.

All this refers still to the simplest cases, where the participation of the musicians can be regulated at will during the experiment. Nevertheless even in the most complicated cases everything depends on the observation of the concordance or difference in the playing of the separate instruments.

In preparing ammonium arsenate Mitscherlich was struck by the similarity of this salt with the corresponding phosphate that he had studied shortly before. Further study brought the proof that what he had become aware of was the concordance of their crystal form.

This realization on Mitscherlich's part which led to the discovery of the relation between composition and crystal form, can be likened to picking out the same instrument in two otherwise completely different orchestras.

The imagination was needed to make that discovery; if the crystal form of the first was not vividly present to him during the observation of the second, the correspondence between them could not have occurred to him.

Even though the imagination is used here in order to bring earlier observations back to mind, it cannot be equated with the memory; their relation is about what the capacity to visualize a person is to that of remembering that person's name.

Not all the means for the elucidation of a causal relation are hereby exhausted. Those discussed so far apply only to cases where we deal with direct linear descent, so to speak: causes on one side, effects on the other. Equally probable is the situation where several observations are all effects of the same unknown cause. Its discovery follows quite different paths, namely by imagining a number of possible causes (hypotheses) and comparing their effects with the facts. The first hypothesis to be tried is likely to lead to discrepancies, the second and third perhaps also, but finally a correspondence between the two will be found; then this possible cause will have become the probable one.

Kepler's investigations of the planets offer excellent examples of this second means for the elucidation of the causal connection, because together with his discoveries he reported also the manner by which he arrived at them.

It would go too far to discuss this in detail; suffice it to point out that Kepler's imagination supplied him with new starting points for 22 years, till he finally found the track of the possible cause, and discovered the laws which now carry his name. It is hardly necessary to mention that the capacity mentioned above played a role in this case.

In summary we find that in the mechanism for the discovery of a causal relationship, the imagination is necessary in five operations:

(1) In the choice of the time or the object of observation.
(2) In the arbitrary modification of the observed.
(3) In the finding of aids that simplify the observation and often only make it possible.
(4) In the observation of concordances or differences among data.
(5) In the setting up of a hypothesis.

This mechanism by itself is not fruitful. The person who possesses all the capacities demanded by it, still remains without any significance, unless he possesses the irresistible urge to use these capacities; and this irresistible urge, expressing itself first as enthusiasm and then as endurance, is often the pursuit of a conception only present in the mind of the scientist, and thus is the result of the imagination. Such conceptions, whether true or false, have worked wonders: the firm faith in the influence of the heavenly bodies on the fate of men, and in the philosopher's stone, have provided astronomy and chemistry immeasurable services.

For 23 years, Faraday, who believed in the interconnection of light and electricity, sought to discover it; he found it in the influence of magnetism on polarized light. This idea had, at least at that time, only very little evidence to support it. And Faraday even says of himself in a letter to de la Rive,[1] "Do not suppose that I was a very deep thinker, or was marked as a precocious person. I was a very lively imaginative person and could believe in the 'Arabian Nights' as easily as in the 'Encyclopedia'."

This leads me to history: the conviction, discussed above, that the imagination plays a role both in the capacity to carry out scientific research and in the need to utilize this capacity, led me to study whether in the case of men well known in the sciences, this capacity revealed itself also in ways other than in their scientific research.

On studying more than two hundred biographies, it turned out that this was in fact the case and to a very large extent.

Artistic Expression of Imagination

As a healthy expression of this imaginative power I have considered the artistic sense. In order that everyone may judge the basis on which I concluded that this sense was present, I will cite here a number of quotations taken from the respective biographies.

Newton. It was also near the end of his sojourn in Grantham that (beside marked success in the art of painting) he developed his talents in poetry. Many products of that period have been painstakingly preserved by amateurs ...[2]

Galileo. He was, in his youth, a great admirer of Ariosto. He knew all the "Orlando Furioso" by heart. He took an active and even a somewhat violent part in the greatest dispute of his times in Italy on the comparative merits of Ariosto and Tasso.[3] Age did not weaken either the art of exposition or the poetic turn one notes in the productions of his youth.[4]

Poisson. At Fontainebleau, he achieved brilliant success in his literary studies, as well as in mathematics. He had a veritable passion for the theatre; this indulgence was expensive but he procured it nevertheless, by depriving himself of dinner every fifth day. He knew by heart Molière, Corneille, and especially the tragedies of Racine.[5] It was thus that he came to be friends with Ducis the poet, Gérard the painter, and Talma, the tragedian ....[6]

Watt. The love of anecdote that our associate showed so agreeably during upwards of half a century to all those around him, developed itself very early. The proof will be found in some lines that I am about to quote and translate from an unedited note given in 1798 by Mrs. Marion Campbell, a cousin and juvenile companion of the celebrated engineer.

"During a journey to Glasgow, Mrs. Watt entrusted her young son James to one of her friends. After a few weeks she returned to see him, but most assuredly not expecting the reception she met with. 'Madam,' said her friend, as soon as she saw her, 'you must hasten to take James back to Greenock. I can no longer endure the state of excitement into which he throws me; I am harrassed by want of sleep. Every night, when the usual hour approaches for the family to retire to bed, your son adroitly contrives to raise a discussion, in the course of which he always finds means to introduce a story; this story is sure necessarily to engender a second, and a third, etc. And these tales whether they be pathetic or comic, are so charming, so interesting, that the whole of my family listens to them with such attention, that a fly might be heard to fly. Thus hours follow hours, without our being aware of it; but the next day I am ready to drop with fatigue. Dear madam, take your son home.'"[7]

Davy. Left to himself, he hunted, fished, travelled to all parts of this picturesque country, trying already to sing of its beauties, for, from childhood on, he had been an orator and poet. His impressions were vividly depicted in his tales: each time he returned to school, his friends surrounded him; they crowded close to him, they forgot about everything in order to hear him tell about what he had just seen. His reading excited him no less than the things he observed; barely had a translation of Homer fallen under his eyes, when he too, began to compose an epic, in which Diomedes was the hero; a composition full of life, of a variety of incidents, and in which was developed a richness of invention and a freedom of execution heralding a true poet.[8]

The above has been stated in order to delineate what we mean by the presence of the artistic sense. The following are the names of those of the two hundred randomly chosen men of scientific fame in whom it was present: Ampère, Bailly, Bonafous, Borda, Boyle, Cassini, de la Condamine, Copernicus, Davy, Delessert, Dupasquier, Descartes, Ebn-Jounis, Faraday, Flamsteed, Galileo, Gesner, Goethe, Hallé, van Haller, Halley, Haüy, both Herschels, Ingenhousz, Kant, Kepler, von Kobell, Lacépède, Lagny, Lalande, Leibniz, Lemery, Leonardo da Vinci, Linnaeus, Malus, Miller, Newton, Palissy, Pascal, Poisson, Ramond, Rousseau, Rumford, Schleiden, Scilla, Schopenhauer, Smithson, Tennant, Tycho Brahe, Volta, Voltaire, Watt. This is a total of fifty-two names, or twenty-six per cent ...

Not-So-Healthy Imagination

So much for the healthy expression of a strong imagination; in second line we want to consider its pathological expression. For I have noticed that not infrequently, examples of the strangest imaginings, superstitions, belief in spirits, hallucinations, and even insanity appear in the biographies. Newton was always afraid that an accident would occur to his coach and held on to the door at all times. Kepler's conceptions about the universe were most peculiar; in all seriousness he believed that the earth was a reptile, and that the planets around the earth brought forth

[1] TYNDALL, J., "Faraday as a Discoverer," Longmans, Green & Co., London, 1868, p. 7.
[2] ARAGO, F., "Oeuvres Complètes," Gide et J. Baudry, Paris, 1855, Vol. III, p. 324.
[3] *Ibid.*, p. 260.
[4] *Ibid.*, p. 286.
[5] ARAGO, "Oeuvres Complètes," Vol. II, 1854, p. 599.
[6] *Ibid.*, p. 602.
[7] ARAGO, "Oeuvres Complètes," Vol. I, p. 376. Translated by SMITH, W. H., POWELL, B., AND GRANT, R., in "Biographies of Distinguished Scientific Men," Ticknor & Fields, Boston, 1859. 2nd series, p. 356.
[8] CUVIER, GEORGES, *Mem. acad. roy. sci.*, 12, iii (1829).

by their motions a melodious harmony (Jupiter and Saturn were basses, Mars tenor, etc.).

Davy, in his "Consolations in Travel or the Last Days of a Philosopher," describes a visit to Saturn in the following words:

> Looking through the atmosphere towards the heavens, I saw brilliant opaque clouds of an azure color, that reflected the light of the sun, which had to my eyes an entirely new aspect, and appeared smaller, as if seen through a dense blue mist. I saw moving on the surface below me immense masses, the forms of which I find it impossible to describe; they had systems for locomotion similar to those of the morse or sea horse, but I saw with great surprise that they moved from place to place by six extremely thin membranes which they used as wings. Their colors were varied and beautiful, but principally azure and rose-color. I saw numerous convolutions of tubes, more analogous to the trunk of an elephant than to anything else I can imagine, occupying what I supposed to be the upper parts of the body, and my feeling of astonishment almost became one of disgust, from the peculiar character of the organs of these singular beings; and it was with a species of terror that I saw one of them mounting upwards, apparently flying toward those opaque clouds which I have before mentioned. . . .[9]
>
> *Descartes.* He often had nocturnal visions, of which he gave interpretations next morning which seemed proof of a complete derangement of his intelligence. . . .[10]

I cite these in order to circumscribe what is to be understood by pathological expressions of the imagination. The names of those of the two hundred arbitrarily chosen men of scientific fame in which it is found follow:

Ampère, *Bailly*, Bonnet, *Boyle*, Crookes, *Davy*, *Descartes*, *Flamsteed*, *Haüy*, *Leibniz*, *Newton*, Priestley, *Ramond*, *Schopenhauer*, Wallace.

Those are fifteen names, of which, significantly, eleven (those in italics) have already been cited in the earlier list.

Now that we have on the one hand pointed to the important role that falls to the imagination among the capacities that make a person into a fruitful scientist, and have established that it occupies that place in history that we suspected, we wish now to make one more comment with respect to our own time.

The number of those occupied with scientific research is increasing. Formerly only an irresistible urge and quite exceptional ability were able to overcome all the obstacles in the way of a scientific career. Today the path lies open and is well-trodden.

However, it follows as a direct consequence, that with increasing numbers the average quality is lower. The rare gifts, among them imagination, move into an unfavorable position with respect to those generally present. This has changed the pattern by which science proceeds. . . .

When imagination is lacking, the attempt is made to make up for this lack in other ways:

(1) The careful choice of object and time can be replaced by systematic observation of all phenomena at every moment; the night sky has been divided among the different observatories, and there is not much that can escape notice; whatever is observed is sent to Strasbourg where it is measured and tabulated.

(2,3) The achievement of a result, through an experiment or through the refinement of the means of observation, can be helped by groping in all directions and by trial and error.

(4) The discovery of relations can be made easier, by expressing observations numerically and comparing the numbers obtained among themselves.

(5) In the end, the hypothesis shimmers so clearly through the countless observations, that its enunciation requires only a small step.

(6) Enthusiasm can be greed for honors.

It is in fact true that by these means the needs are sufficiently met; the results prove it. But scientific discovery has now become something other than it formerly was; it now resembles the shooting up of a fortress from several sides, the cautious ascent of the ruins and the battle to hoist the flag as all reach the summit together. It used to resemble the simple shift of a single battery, like that with which Napoleon managed to overcome the British fleet at Toulon. Although the imagination can now be replaced by the sacrifice of a great amount of labor, it is not excluded; the role it plays has changed; it is not the role that it is capable of playing; even today Kepler would have been able to raise himself as high above his surroundings as in his own time.

Cuvier once compared, at the end of a biography, two great chemists, Vauquelin and Davy. He there expressed himself something like this:

> In spite of his countless researches, in spite of the important and strange discoveries with which Vauquelin enriched science, he can not be put on the same level with Davy. The former put his name into the paragraphs, the latter into the titles of every chapter. The former, in all modesty, observed with a lantern the most hidden places, and penetrated into the darkest corners; the latter rose up like an eagle and illuminated the great region of physics and chemistry with a burning torch.[11]

These words I make my own in order to describe what research is without imagination, what it can be when the imagination is properly used. Vauquelin was not named in the compilations cited above, Davy in both, as poet and also as visionary. His discoveries were the fruit of that great gift which Buckle describes:

> There is a spiritual, a poetic, and for ought we know a spontaneous and uncaused element in the human mind, which ever and anon, suddenly and without warning, gives us a glimpse and a forecast of the future, and urges us to seize truth as it were by anticipation.[12]

[9] DAVY, SIR HUMPHRY, "The Collected Works of Sir Humphry Davy," Smith, Elder & Co., London, **1840**, Vol. 9, p. 241.

[10] ARAGO, "Oeuvres Complètes," Vol. III, p. 299.

[11] Cuvier, *op. cit.*, **12**, lvi (1829).

[12] BUCKLE, HENRY THOMAS, "Miscellaneous and Posthumous Works," Longmans, Green & Co., London, **1872**, Vol. I, p. 15.

NBS Wavenumber Tables Published

NBS Monograph 3 in two volumes was issued in May, 1960. Volume I (500 pages) covers the range 2000–7000 Å; volume II (534 pages), 7000 Å-1000 μ. Tables convert wavelengths in air to wavenumbers in vacuum. Each volume is priced at $6.00, available from U. S. Government Printing Service, Washington 25, D. C.

Ford R. Bryan
Ford Motor Company
Dearborn, Michigan

Polaroid Films Simplify Instruction in Spectrographic Analysis

Laboratory instruction in spectrographic analytical methods has been seriously handicapped by the need for rather elaborate darkroom facilities and considerable student training in photographic processing techniques. As a result, courses in spectrographic analysis can be afforded only by comparatively large schools, and class enrollments must be limited to relatively small numbers. Since conventional photographic processing is time-consuming and somewhat incidental to the underlying principles of spectroscopic analysis, a means of simplifying the photographic process is important from the standpoint of efficient teaching.

Polaroid emulsions can be used to demonstrate both qualitative and quantitative analysis by modifying a conventional spectrograph to accomodate Polaroid film. The experiments to be described involve the use of Polaroid positive prints and are designed to illustrate a simple means of utilizing one-step photographic processing[1] in a system appropriate for laboratory instruction.

Equipment

Spectrograph, source, and recording medium are selected to be compatible with one another in degree of usefulness. The spectrograph which has been used is a medium dispersion, glass prism instrument[2] with mechanically limited range of 3700 to 6500 Å. The transmission of glass and the spectral sensitivity of Polariod emulsions extend to nearly 3000 Å, however. The spectrograph's upper limit of wavelength range coincides with the emulsions's limit of 6500 Å. The region in the neighborhood of 4000 Å is especially useful for alloy analysis. In this region dispersion is approximately 4 Å per mm, and 400 Å can be photographed in a single exposure. Several exposures can be recorded on one photographic frame. The spectrograph camera is modified to accomodate a Polaroid film holder for Professional Pan, Type 53, in 4 × 5 Film Packet size. Separate frames are thus loaded, exposed, and processed individually.

An A.C. arc generator provides adequate sensitivity and reproducibility for demonstration of both qualitative and quantitative spectrochemical applications. The arc circuit is equipped with an ignitor and ballast resistor and operates from standard 110 or 220 v outlets. The complete arrangement of equipment can be accommodated on a 4-ft. bench space as illustrated in Figure 1. Although apparatus of this type is less elaborate than the high precision facilities used for industrial analysis or university research, it offers order of magnitude benefits in initial costs and in experimental time required to demonstrate basic principles.

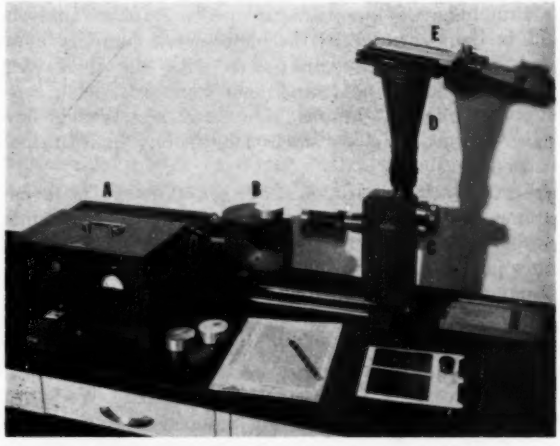

Figure 1. Complete spectrographic equipment: *A*, arc ignitor; *B*, specimen stand; *C*, spectrometer; *D*, camera; *E*, Polaroid film holder.

Use in Analysis

A simple arc source together with a low dispersion spectrograph is satisfactory for the qualitative identification of metals. Excitation need not be especially stable for producing qualitative spectra, and spectral range is often more important than high dispersion. A supply of Johnson-Matthey pure metals and a copy of the MIT Wavelength Tables will serve to establish the identity of lines.

Figure 2 illustrates spectra of three commercial alloys recorded in the near ultraviolet on the Polaroid, Type 53, emulsion. Both major and minor constituents can be identified by selection of arc current and exposure time. A one-minute exposure reveals the trace of iron impurity in the aluminum alloy. The alloying elements, copper and magnesium, are also apparent in the aluminum. The copper alloy contains several per cent aluminum which classifies it as an aluminum bronze. The magnesium metal, containing alloyed aluminum, is found to be relatively free of impurity elements in this region. The dispersion, range, and sensitivity of this equipment combined with the Polaroid emulsion are exceptionally well suited to rapid qualitative metallurgical analysis.

[1] Land, E. H., *J. Opt. Soc. Am.*, **37**, 61–77 (1947).
[2] Metal-Spectroscope manufactured by R. Fuess. Distributed in the United States by Applied Research Laboratories, Glendale, California.

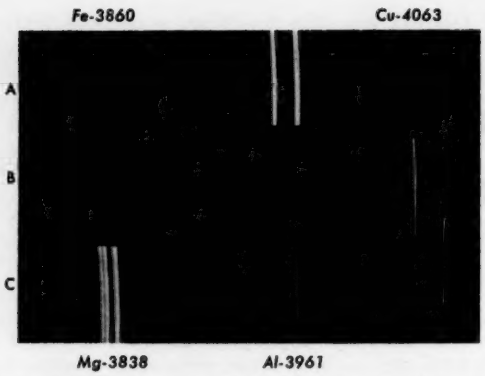

Figure 2. Qualitative arc spectra of commercial alloys recorded on polaroid film: *A*, aluminum alloy; *B*, aluminum bronze; *C*, magnesium alloy.

Principles of quantitative spectrographic analysis can be demonstrated by the photometric comparison of line intensities from unknowns with the intensities of corresponding lines from known standards. The concepts of internal standard lines and homologous line pairs[3] are essential considerations in any quantitative procedure.

Of the various methods of line photometry, the measurement of line height as produced by a logarithmic wedge[4] seems attractive, since the spectra are produced on a paper-based emulsion and cannot be measured by standard transmission densitometry. Either the logarithmic sector disc or a neutral filter of the continuous logarithmic wedge type is appropriate when placed immediately adjacent to the spectrograph entrance slit. For this work, a Wratten Neutral Density Wedge of 5-cm size was photographically reduced on fine-grained film to 15-mm dimensions and placed over the entrance slit to provide a density gradient of 0.0 to 2.0 along the length of the slit. Resulting spectral lines are thus tapered in appearance, and the difference in lengths[5] of two lines within a spectrum is proportional to the logarithm of the ratio of the line intensities. A simple magnifying glass with millimeter scale provides line height measurements reproducible to the nearest 0.5-mm value.

An example of quantitative calibration utilizing this simplified spectrographic procedure is illustrated by means of a series of steel standards containing chromium ranging from 0.006% to 2.40% by weight. Each standard was excited for a period of 15 sec by means of a 4-amp A.C. arc. The spectra were recorded in the 4200–4300 Å region where several sensitive chromium lines exist (Fig. 3). The heights of the CrI 4289.7 Å line and the FeI 4292.3 Å line were measured, and the difference in line heights determined for each standard. A listing of the standards together with the corresponding line heights and differences obtained is shown in Table 1. Importance of the internal standard principle is observable in Table 1. Chromium concentrations which are indistinguishable by means of chromium line heights alone are reliably separated by consideration of the corresponding iron reference line heights.

A graphical relationship between differences in line heights and chromium concentration may be presented as in Figure 4. This form of calibration curve emphasizes the inherent non-linearity of spectral response to concentration and graphically illustrates the high sensitivity of the spectrographic method at relatively low concentrations. From Figure 4 it is also quite apparent that a constant photometric error produces a widely varing absolute error in concentration when the entire concentration range is considered.

A more conventional analytical calibration curve is a plot of the logarithm of the ratio of line intensities versus the logarithm of element concentration. This version of the same data is shown in Figure 5. The

Figure 3. Quantitative spectra of steels recorded through a logarithmic wedge on Polaroid film.

difference in line heights, as determined by the optical wedge function, represents the logarithm of the intensity ratio; the concentration is then plotted on a logarithmic scale. The expected linear relationship is thus obtained over approximately three orders of magnitude concentration. From this type of calibration it is apparent that a given photometric error results

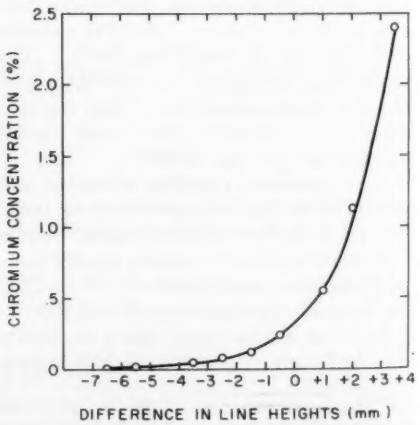

Figure 4. Response of the Cr I 4289.7 Å and Fe I 4292.3 Å line pair with changes of chromium concenatrtion in steel.

[3] GERLACH, W., SCHWEITZER, E., "Foundations and Methods of Chemical Analysis by the Emission Spectrum," Adam Hilger, Ltd., London, **1931**.

[4] SCHEIBE, G., NEUHÄUSSER, A., *Angew. Chem.*, **41**, 1218 (1928).

[5] TWYMAN, F., AND SIMEON, F., *Trans. Opt. Soc.*, **31**, 169–183 (1929–30).

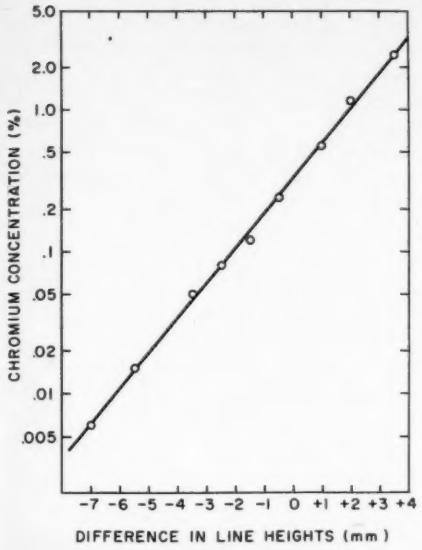

Figure 5. Conventional analytical calibration curve for chromium in steel using arc excitation, wedged line photometry, and Polaroid emulsion.

in a constant error throughout the concentration range in terms of percentage of the amount of element present in the sample.

In this quantitative procedure the error in matching line heights, which approaches a 0.5 mm maximum is believed to be the limiting factor in accuracy of the method. In this case of chromium in steel, the error averages about ±10% of the amount of chromium in the sample. Refinements in photometry could perhaps reduce error to within ±5%.[6] As with spectrographic methods in general, the degree of accuracy obtainable is most advantageous at low concentrations.

Table 1. Quantitative Photometric Data

Chromium concentration (%)	Chromium line height (mm)	Iron line height (mm)	Difference line heights (mm)
0.006	5.0	11.5	−6.5
0.015	5.5	11.0	−5.5
0.05	7.5	11.0	−3.5
0.08	9.0	11.5	−2.5
0.12	9.0	10.5	−1.5
0.24	11.0	11.5	−0.5
0.55	12.5	11.5	+1.0
1.14	12.5	10.5	+2.0
2.40	14.0	10.5	+3.5

Conclusions

Spectrographic analysis, both qualitative and quantitative, can be accomplished with comparatively simple equipment and without a darkroom, by the utilization of Polaroid-Land films. Range and accuracy of the methods are appropriate for demonstration of the basic principles of emission spectrochemical analysis of metals and alloys. Savings in equipment costs and experimental time over conventional spectrographic procedures are sufficient to warrant inclusion of spectrochemical instruction in many more chemical and metallurgical courses.

[6] Green, M., and Polk, M. L., *Appl. Spectroscopy*, **8**, 126–30 (1954).

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Acid-Base Titrations with the Tellurium Electrode

Hydrogen ion activity in aqueous solutions can be determined potentiometrically using various indicator electrodes. Those that are most commonly used are the hydrogen electrode, the glass electrode, organic redox electrodes notably the quinone-hydroquinone system, and metal-metal oxide electrodes. The reversible oxidation potential of a metal-metal oxide electrode as a function of *p*H was formulated by Fenwick and Roberts (*1*). The potential for the tellurium-tellurium oxide electrode can be deduced by considering the following equilibria

$$TeO_2(s) + 2H_2O\ (1) \rightleftarrows Te^{+4} + 4OH^-$$

for which the equilibrium constant is

$$K_1 = \frac{a_{Te^{+4}}\, a_{OH^-}{}^4}{a_{TeO_2} a_{H_2O}{}^2}$$

$$2H_2O\ (1) \rightleftarrows H_3O^+ + OH^-$$

for which the ion product is

$$K_w = a_{H_3O^+}\, a_{OH^-}$$

The potential of a tellurium electrode in contact with a solution of its ions is given by the Nernst equation

$$E = E^\circ - \frac{2.303\, RT}{4\, \mathfrak{F}} \log a_{Te^{+4}} \qquad (1)$$

Provided that the only source of tellurium ions in solution is through ionization of its oxide with which the solution is saturated, the activity of the tellurium ions is governed by the equilibrium constant K_1 and hence the activity of the hydroxide ion. Substituting for the activity of the tellurium ions in equation (1) and assuming unit activity for the solvent gives

$$E = E^\circ - \frac{2.303\,RT}{4\mathfrak{F}} \log \frac{K_1}{K_w^4} - \frac{2.303\,RT}{\mathfrak{F}} \log a_{H_3O^+} \quad (2)$$

Thus the reversible oxidation potential of the tellurium-tellurium oxide electrode should be a linear function of pH,

$$E = E^{\circ\prime} + \frac{2.303\,RT}{\mathfrak{F}}\, p\mathrm{H} \quad (3)$$

$E^{\circ\prime}$ is a constant characteristic of the electrode reaction, and the other terms have their usual significance (*2*). For the tellurium-tellurium oxide electrode Tomíček and Poupe (*3*) report the relationship

$$E = -0.603 + 0.058\ p\mathrm{H} \quad (4)$$

at 20° in the pH range 0 to 9 while Ricketts and Tresselt (*4*) report the relationship

$$E = -0.593 + 0.0469\ p\mathrm{H} \quad (5)$$

at 25° in the pH range 2.2 to 8.0.

The irreproducibility of metal-metal oxide electrodes is well known; consequently, they cannot be used in general for the accurate determination of pH. In the case of the antimony-antimony oxide electrodes reported $E^{\circ\prime}$ values range between 0.151 and 0.200 v, while the slopes of the potential versus pH curves range betweeen 0.043 and 0.0647 v (*5*, *6*). However, since metal-metal oxide electrodes afford a system of rugged construction, of low internal resistance, and one not easily poisoned, they can be used advantageously in acid-base titrimetry.

In this laboratory the student titrates the given acid-base pair simultaneously using both a tellurium electrode and a glass electrode to indicate pH changes during the titration. Not only is he introduced to two indicating electrode systems but in addition he is able to compare their performances.

The Experiment

Two types of tellurium electrodes, a cast electrode or an electrodeposited electrode, are suitable. The cast tellurium electrode is prepared as described in the literature (*7*) except that it is vacuum cast directly onto a platinum wire lead. Electrodeposited electrodes are more simply prepared and perform more satisfactorily in the titrations; consequently, their preparation will be described. The plating bath is a 5% solution of sodium carbonate saturated with TeO_2. The cathode may either be a platinum foil or a platinum wire electrode; a stick of tellurium serves as anode. The cathode is plated for 5 min. at −0.75 v at a current density of 0.008 amp per cm². This initial plate is necessary since the simultaneous deposition of hydrogen is detrimental to the adherence of the tellurium coating. The cathode potential is then changed to −2.00 v and plating is continued until the surface is covered with an amorphous coating of tellurium. At the conclusion of this plating procedure the electrode has much the same appearance as does a platinized platinum electrode. Prior to their use in titrations the electrodes may be satisfactorily stored in distilled water.

Table 1. Comparison of Tellurium and Glass in Acid-Base Titrimetry

Tellurium electrode number	Ml base required with Te	Ml base required with glass	Acid
1	26.53	26.50	HCl
2	26.45	26.50	HCl
1	26.40	26.40	HAc
2	26.40	26.40	HAc
3	35.25	35.25	HCl
3	35.24	35.21	HCl
4	35.27	35.25	HCl
4	35.29	35.21	HCl
3	33.33	33.20	HAc
4	33.22	33.20	HAc
5	35.62	35.66	HCl
6	35.62	35.66	HCl
7	35.69	35.66	HCl
5	33.25	33.30	HAc
6	33.24	33.30	HAc
7	33.42	33.30	HAc

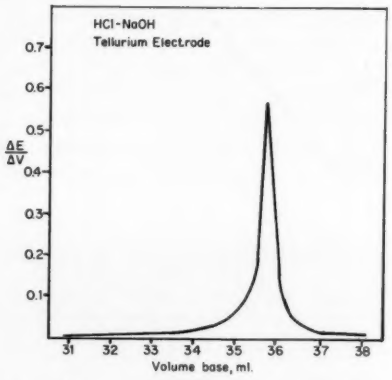

Figure 1.

In each of the titrations 25 ml of the acid (0.1 *N*) were diluted to 300 ml with distilled water and then titrated with sodium hydroxide solution of approximately the same concentration as the acid. The course of the titration was followed using a glass-saturated calomel electrode couple in conjunction with a Beckman Model G pH meter and also a tellurium-saturated calomel couple in conjunction with a Leeds and Northrup Portable Potentiometer Electrometer. The titrations were run at room temperature; the solutions were stirred magnetically. To realize a stable emf the potential difference of the tellurium-calomel couple was not measured until 2 min. after the addition of each increment of base. This 2-min. period seems to be minimum time necessary for stabilization and varies markedly from the findings of both St. de Brouwer (*8*) and Bravo (*9*) who found a 2–3 hr. stabilization period was required.

The table summarizes the results of the titrations. The equivalence point in each case was obtained from a differential plot of the data. Three separate series of titrations were performed. Since in each case freshly prepared solutions of both acid and base were employed, the results are expressed as ml base necessary to neutralize the 25-ml acid sample. Electrodes 1 and 2 were cast tellurium; electrodes 3 and 4 were platinum foil electrodes that were freshly plated with an amorphous tellurium coating just prior to the titration. Electrodes 5, 6, and 7 were platinum wire electrodes plated with an amorphous coating of tel-

lurium and then stored in distilled water for three weeks before being used.. Their behavior during the titrations was remarkably reproducible; the potentials of each of these electrodes deviated from each other by less than 0.01 v. Figure 1 shows a differential plot of the titration of HCl-NaOH for these wire electrodes (the three separate curves are superimposable).

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(1) Fenwick, F., and Roberts, E., *J. Am. Chem. Soc.*, **50**, 2145 (1928).
(2) See, for example, Kortum, G., and Bockris, J. O'M., "Textbook of Electrochemistry," Elsevier Publishing Company, New York, N. Y., **1951**, p. 293.
(3) Tomíček, O., and Poupe, F., *Collection Czechoslov. Chem. Commun.*, **8**, 520 (1931).
(4) Ricketts, J., and Tresselt, L., *J. Am. Chem. Soc.*, **81**, 2305 (1959).
(5) Stock, J., Purdy, W., and Garcia, L., *Chem. Revs.*, **58**, 611 (1958).
(6) Tourky, A., and Moussa, A., *J. Chem. Soc.*, 752 (1948).
(7) Ricketts and Tresselt, *op. cit.*
(8) de Brouwer, S. *Bull. soc. chim. Belg.*, **48**, 158 (1938).
(9) Bravo, A., *Ann. chim. applicata*, **26**, 162 (1936).

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A Universal Azeotropic Water Separator

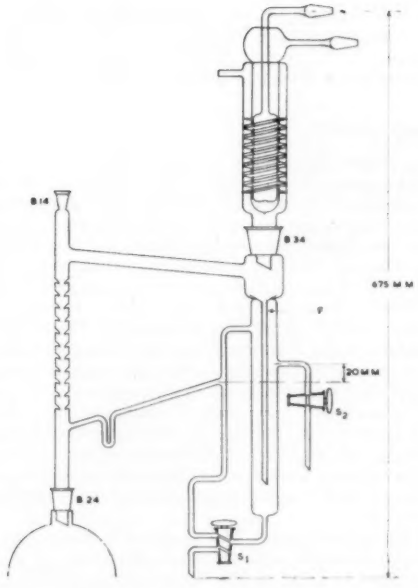
Apropos of the description of a universal steam distillation apparatus,[2] we wish to communicate a description of a universal azeotropic water separator (see figure) which has been developed in these laboratories and has been in routine use for over a year now.

The Dean-Stark apparatus for lighter-than-water entrainers has been in common use since its description in 1920.[3] Cork-and-glass assemblies employing heavier-than-water entrainers have been described in the "Organic Syntheses" volumes.[4] The present apparatus is a modification of a compact all-glass version described by Sukh Dev.[5]

When employing a lighter-than-water entrainer the stopcocks S_1 and S_2 are closed. As the reaction proceeds, the transported water is run out from time to time by setting S_1 to communicate with the outlet.

When operating a heavier-than-water entrainer S_1 is set to allow the solvent to flow into the feedback tube to be returned to the reaction vessel. Water overflows through S_2 when a layer of about 2 cm (20 ml) has been built up.

The apparatus has proved itself eminently satisfactory when employed on preparations on scales met with in the "Organic Syntheses" and on many reactions requiring water removal in academic research (dehydration of materials, ketalization, esterification, Cope-Knoevenagel condensations, etc). It has, however, not yet been strictly evaluated. It is realized



that skill in glass blowing is necessary for making it. But since the design is diagrammatic it is thought that it would be valuable as a teaching aid. The only critical dimension is the height difference of 20 mm between outlet and feedback tubes; a thermometer well (B 14) or a B 14 stopper closes the head of the column which should be lagged; the funnel *F* usually has enough irregularity near where it rests to allow equalization of pressure; otherwise a hole of 3-mm diameter should be made in the conical part.

The author wishes to thank Professors Dilip K. Banerjee, B. H. Iyer, and S. Dev of the department of organic chemistry, Indian Institute of Science, for their interest in its development and S. K. Satyanarayana, glass technician, for making prototypes.

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[2] Wallenberger, F. T., O'Connor, W. F., and Moriconi, E. J., J. Chem. Educ., **36**, 251 (1959).
[3] Dean, E. W., and Stark, D. D., *Ind. Eng. Chem.*, **12**, 486 (1920).
[4] *E.g.*, Clarke, H. T., and Davis, A. W., in "Organic Syntheses," Coll. Vol. I, 2nd ed., John Wiley & Sons Inc., New York, 1946, pp. 261, 421; Adams R., and Marvel, C. S., *Ibid.*, p. 368.
[5] Dev, S. *J. Indian Chem. Soc.*, **30**, 668 (1953); also a modification with provision for drying the returning entrainer; *Ibid.*, 30, 447 (1953).

Division of CHEMICAL EDUCATION
American Chemical Society

Summary of Problems and Progress in Chemical Education

EDITOR'S NOTE: The following report was made to the Committee on the Teaching of Chemistry of the Division of Chemical Education, ACS, by the chairman at the Cleveland meeting, April, 1960. It covers the whole "front" in the continuing effort of so many to improve the training of chemists and potential chemists. The committee is hard working and far reaching in its activities. Readers of THIS JOURNAL owe themselves the news of what is going on and owe the Committee their support.

In planning its work for the improvement of chemical education the Committee on the Teaching of Chemistry has four main concerns: the definition of course content; the preparation of new teachers; opportunities for practising teachers to broaden and deepen their understanding of chemistry; the availability teaching aids.

These four concerns are related to chemical education at five levels: elementary schools (kindergarten through sixth grade); junior high schools (grades seven through nine); senior high schools (grades ten through twelve); junior colleges; four-year colleges.

Elementary Schools

In the elementary schools chemical education is necessarily a part of programs of education in all the sciences. Course content is determined by school boards and their staff of educators (including teachers and supervisors) with varying degrees of prescription from school agencies above the local school board. The National Science Teachers Association, a unit within the National Education Association, is actively engaged in a program called "K-12"—a study which will result in recommendations for course content from kindergarten through the twelfth grade. The members of the American Chemical Society should keep informed of progress in this study and stand ready to offer suggestions concerning course content in chemistry at whatever level they feel competent to deal with. Through participation in the activities of their local boards of education and through their Local Section Committees on Education, the members of the Society have ready lines of communication for participating in the development of a modern approach to science education in the public schools.

The Committee on the Teaching of Chemistry has a subcommittee concerned with chemical education in elementary schools. The chairman of this subcommittee is Noel Simmons who teaches chemistry in New York's State University College for Teachers at Buffalo. Through his efforts, and those of other members of his subcommittee, we hope to gather data on what aspects of chemistry should be included in elementary school science, what chemistry should be included in the training of elementary school teachers, and what teaching aids are needed for practising teachers.

In connection with the last category, it is gratifying to note the production, publication, and large scale distribution by the Manufacturing Chemists Association of the booklet, "Matter, Energy, and Chemical Change—Explorations in Chemistry for Elementary School Children." This booklet should be read by every chemist concerned with improving elementary education in chemistry and its contents drawn to the attention of local school teachers and administrators. It is obtainable from Holt, Inc., 383 Madison Ave., New York 17, N. Y., for fifty cents.

Although the National Science Foundation has already made grants for several institutes to help elementary school teachers do a better job in teaching science, every local section of the Society should be concerned with this problem and supplement such institutes with projects in its own area. Only a nation-wide, grass roots movement can possibly cope with the tremendous problem of improving education in science in our elementary schools.

Junior High Schools

As far as junior high schools are concerned, course content in chemistry has been largely determined by local school systems with some assistance from boards of education with wider responsibilities. The NSTA K-12 program mentioned previously will provide much help in determining course content but local sections of the Society can be of great assistance in their communities. At present, the Committee on Teaching has no subcommittee concerned with this area of interest and the chairman will welcome offers of assistance. The Committee hopes that the MCA will proceed with the development of aids to teachers at this important level of education in chemistry. Some help toward improving the background of junior high school teachers is becoming available to them through participation in NSF institutes.

Senior High Schools

Activities to improve chemical education in the senior high school now far exceed the sum of efforts for improvement at all other levels. Several groups of chemistry teachers have published course outlines in the JOURNAL OF CHEMICAL EDUCATION and *The Science Teacher*—published by NSTA. The National Science Foundation is supporting two major programs for the improvement of course content: The Chemical Bond Approach Committee (CBAC) now centered at Earlham College and directed by L. E. Strong and the Chemical Education Materials Study (CHEMS) under the leadership of Glenn Seaborg with direct supervision by J. A. Campbell at Harvey Mudd College. Several colleges of education (among them the college at the Ohio State University and Teachers College of Columbia University) and other groups of educators are working toward the development of integrated high school courses including biology, chemistry, earth sciences, and physics. High school chemistry syllabi are frequently recommended or prescribed by state and local boards of education.

Curricula recommended for the preparation of secondary school teachers of chemistry have been prepared by several organizations including the AAAS Cooperative Committee on Teacher Certification under the chairmanship of A. B. Garrett. The recommendations of this committee are now being studied by the National Education Association's Commission on Teacher Education and Professional Standards (TEPS). In this connection, too, there is need for grass roots activity by local sections of the Society to bring the recommendations of the Cooperative Committee to the attention of educational policy makers in their communities.

Efforts to broaden and deepen high school teachers' understanding of chemistry center around the NSF program of in-service, academic year, and summer institutes. The ACS Chemical Education Division's Committee on Institutes and Conferences under the chairmanships of J. F. Baxter, W. B. Cook, and W. T. Lippincott in succession has performed tremendous services in helping colleges and universities develop such institutes. The Division's Committee on Teaching had a subcommittee under the chairmanship of W. B. Cook which published a report (J. CHEM. EDUC., 35, 417 (1958)) drawing attention to the many special programs at various universities leading toward a master's degree in the teaching of science. NSF programs of successive summer institutes and "Continental Classroom" (sponsored by the Society and other organizations interested in chemical education, presenting John F. Baxter in a television program of Modern Chemistry designed especially for high school teachers who wish to improve their competence in chemistry) are further aids to teachers.

Numerous teaching aids for high school chemistry teachers have been developed. The Division of Chemical Education's high school chemistry test was prepared by a group under the aegis of the Division's Committee on Examination of which T. A. Ashford is chairman. Bayes Norton and his fellow workers have done much to improve high school chemistry through developing and promoting the advanced placement program and examinations. NSTA has also prepared high school examinations. Additional examinations are being prepared by the CBAC. Films and film strips have been prepared by McGraw-Hill and Encyclopedia Brittanica, the latter collection of 160 films for a complete high school course having J. F. Baxter as the lecturer. Films have also been prepared by E. C. Weaver with the support of the MCA. The ACS Board of Directors' Committee on Films with A. B. Garrett as chairman is exploring the need for new films. Directions for laboratory experiments have been prepared and distributed by MCA and CBAC. The JOURNAL OF CHEMICAL EDUCATION publishes much material of value to the high school teacher in his classroom and laboratory. The *National Science Teacher* also publishes such material. Special efforts like the program of "Industry Aids to Education" sponsored by the New England Council for Economic Development, the grass roots approach of the Joe Berg Foundation, and the Southern California Industry-Education Council have also provided teaching aids to many high schools. The Science Teaching Improvement Program (STIP) sponsored by AAAS has also rendered valuable service to chemical education. Tremendous services to improve chemical education in high schools have been rendered by local sections and these need to be continued and expanded if the great goal of sound chemical education in our high schools is to be achieved.

Junior Colleges

The rapid growth of junior colleges is posing new problems in chemical education. Because many junior college teachers and administrators are drawn from secondary schools many educators consider junior college to be essentially an extension of secondary school into the thirteenth and fourteenth grades. To implement this point of view they design terminal curricula and treat their teachers as upper level high school personnel. On the other hand, four-year college teachers expect junior colleges to give fundamental courses upon which upper level college courses can be based. There is little doubt that junior colleges need to offer both terminal and fundamental courses. There is also little doubt that the latter will serve as effective preparation for more advanced chemistry only if teachers from four-year colleges work with junior college teachers in recommending course content. The Committee on Teaching has a subcommittee on junior college chemistry serving under the chairmanship of Roger A. Max, Chairman of the Science and Mathematics Department at Flint (Michigan) Junior College. Junior college teachers and four-year college teachers are members of this subcommittee. This subcommittee is gathering data on chemical education in junior colleges. When these data are assembled they will guide the committee's future activities. It is already apparent that we need summer conferences especially designed to bring together junior college chemistry teachers and teachers of first and second year chemistry in the four-year colleges. The junior college chemistry teacher needs the sympathetic support of the professional chemist in order to develop the kind of course which will prepare his students for further work in our field. Chemists in communities having junior colleges should make themselves aware of what chemical education is being offered and how it can be improved. Here, again, the local sections can perform valuable services.

Four-Year Colleges

Curricula in chemistry in our independent colleges of liberal arts and sciences are in a state of flux unprecedented in the twentieth century. Through programs at ACS National Meetings, promotion of institutes, conferences, and regional associations, publication of the JOURNAL OF CHEMICAL EDUCATION, activities of committees and individuals, the members of the Society and its Division of Chemical Education have contributed to a ferment of growing potency. New content has been introduced into first-year courses with concomitant changes in the courses which follow. Organic chemistry, quantitative and qualitative analysis, elementary physical chemistry, and physics have been blended in various proportions with the traditional inorganic chemistry to serve as the factual foundation on which to build a structure of basic principles in chemistry.

Through its support of special conferences on course content for the four-year curriculum in college, the National Science Foundation has done much to promote the emergence of new ideas about teaching college chemistry and new ways of implementing them. The conference in June of 1959 at Harvey Mudd College brought together teachers from liberal arts colleges and universities to discuss the correlation of undergraduate and graduate instruction in chemistry. A conference at Wooster College in the summer of 1959 produced a detailed report pointing out how research by teachers and students in undergraduate colleges stimulates higher achievement in chemistry. The National Science Foundation is promoting research by college teachers through Faculty Fellowships and through its program of grants enabling students and teachers in small colleges to participate in special research programs either on their own campuses or at various universities. A conference at Bucknell University in June of 1960 explored ideas for further improvements in undergraduate instruction in chemistry. A conference at Montana State College in July of 1960 was concerned with the teaching of chemistry to students with a major interest in applied science such as agriculture, nursing, etc. The program of Visiting Scientists in Chemistry financed by the National Science Foundation and administered by a committee of the Division of Chemical Education is furnishing new stimuli toward better chemical education.

Conclusion

In preparing a summary like this it is inevitable that the writer will fail to include all that he should. For these sins of omission, the author asks forgiveness. In the same breath he request that such sins be brought to his attention so that due penance may be performed through a better summary at some future date. Though the scientific community in general and chemists in particular are making contributions of great value to the cause of improving chemical education, we must not relax but extend our efforts. The Committee on Teaching of the ACS Division of Chemical Education welcomes suggestions concerning programs to be developed and offers of help to implement them.

EDWARD C. FULLER, *Chairman*
Committee on the Teaching of Chemistry
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King's College
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Chemistry-Teaching Conferences in the Washington, D. C., Area

As part of a program of science education financed by a grant from the National Science Foundation, the Washington Academy of Sciences held, during the fall and winter of 1959–60, a series of conferences on chemistry teaching in the secondary schools. Participants included high school teachers of chemistry, members of the chemistry departments of local universities and colleges, and chemists from neighboring industrial and government laboratories.

The conferences consisted of all day meetings with a threefold agenda—the relation of the high school chemistry course to college preparation; problems in the teaching of college chemistry owing to high school preparation; how to provide better liaison between high school teachers, college instructors, and the scientific community.

Since the national capital area represents two states and the District of Columbia, three preliminary conferences were held, one in each political area. To encourage a broad base of participation, attendance at each conference was limited to 10 persons from each of the three mentioned professional groups. Conferences were held from 9:00 A.M. to 4:00 P.M., with luncheon provided from the NSF grant. Locales for the meetings were the Universiy of Maryland, the Northern Virginia Center of the University of Virginia and the American University in the District of Columbia.

The concluding or summarizing conference held on February 13, 1960, had the distinction of being the first meeting to be held in the auditorium of the new American Chemical Society Building. It followed the same pattern as the earlier conferences except that participants were selected from attendees at the previous meetings to insure a good geographical distribution. Representatives from the American Chemical Society and from the ACS Division of Chemical Education also participated.

The seven major topics discussed were: the objectives of high school chemistry courses; the purpose of, and methods used in, the laboratory; the use of text books; teacher training; the problem of the non-college-oriented student; mathematics and problem solving in chemistry; and intercommunication between and among high school teachers, college teachers and the professional scientists of the community.

Objectives of High School Chemistry

The first topic to be discussed was the objectives of the high school chemistry course. These include understanding of the basic ideas (laws and principles) of chemistry, ability to write equations, ability to think dimensionally, the understanding of chemistry as a science rather than as a compilation of items to be memorized, an understanding of descriptive chemistry with the qualification that principles are important and descriptive facts serve best to illuminate the principles and, most important, the inculcation of an enthusiasm for chemistry.

The relation between enthusiasm and the other objectives was discussed at length. It was stated that enthusiasm as such is not fruitful unless the student knows what he is enthusiastic about. Specifically, purposeful enthusiasm can be generated by laboratory work, by proper emphasis in the classroom upon facts that have meaning to the student (the mere mention of *spdf* notation in the classroom, mere exercise in calculations of molarity, molality and normality, were cited as poor examples). Or, in other words, facts, theories, principles, mathematical exercises, and other similar topics must be brought before the student in a way that will help the student to understand why and how these are useful, how they are appropriate to the subject of chemistry.

Later in the day, in connection with discussions on laboratory work, proficiency in mathematics as an objective was mentioned. Thus, many students know how to calculate percentages when given a problem from the book, but when required to perform the same operation upon laboratory data that they have themselves collected, they are unable to apply this knowledge. Hence, it is legitimate to have as an objective of high school chemistry courses the inculcation of an ability to solve mathematical problems in chemistry.

Related to this discussion is the question of preconditioning of students. From their previous experiences in school, most students expect the answer to "come out even"; they expect to observe the exact phenomena in the laboratory that are described in their textbooks and laboratory manuals; they expect to find, from their laboratory data, all those numbers that are needed, and no other numbers, to calculate the necessary numerical answer. When the phenomena do not appear as "expected," when too few, or too many, numbers are obtained, many students flounder.

In order to solve this difficulty, several methods can be used. Thus, students can be given problems with insufficient data and asked to identify the type of information needed to solve the problem. Additionally, teachers will find a full discussion of several methods that can be taught to their students who need to learn the technique of problem-solving in "How to Solve It."[1] The conferees agreed with one teacher who stated that many students could solve problems in chemistry if they could be persuaded that it is *necessary* that a problem be solved. Too often, the student is unable to

[1] POLYA, G., Doubleday Anchor Book, No. A93.

solve a problem not because it is beyond his ability, but because it is beyond his ambition. It is not a simple matter to persuade the student of the necessity that a problem be solved, but it can be done to some extent by emphasizing the importance of the grade to be earned for the course, by challenging the student's sense of self-importance, by developing a milieu in which it is unpleasant to fail to solve an assigned problem, and, no doubt, by still other methods. In the laboratory definite steps can be taken to give students open-end experiments such as those published by the Manufacturing Chemists Association or other similar problems listed in "Practice in Thinking."[2]

Mention of open-end and of the "research" type of laboratory experiment brought forth differing opinions. All seemed to agree that this type of laboratory work would indeed serve to increase enthusiasm and to help the students learn how to apply mathematics to chemistry but some conferees thought that this kind of laboratory work would not help the student to pass his college board examinations, and as one high school teacher stated, "We must always remember the college boards."

Additionally, the use of these preferred types of experiments is time-consuming. Most high schools have fifty minutes for a laboratory period, and this is insufficient even for preplanned, cook-book experiments in many cases.

One teacher who uses open-end experiments stated that she had found them to be very helpful but that it was first necessary to assign a few experiments of the cook-book variety to the students so that they could become familiar with laboratory work in easier stages. Another suggested that the use of semimicro experiments reduced the time needed for set-ups and for dismantling of equipment, thereby increasing the utility of the brief time available in the laboratory period. Lastly, it was suggested that de-emphasis of quantitative experiments and additional emphasis upon qualitative experiments will relieve some of the pressure due to short laboratory periods.

The question of textbook use was first mentioned in connection with the remarks on college boards and was also discussed at intervals thereafter during the conference. Broadly, the conferees seemed to be divided into two groups, those who favored the use of one textbook, with intensive study of that one textbook, and others who favored the use of one textbook with supplementary reading and study of other textbooks and of more advanced reference works. Arguments in favor of one textbook seemed to be centered upon two major points, that it is sufficient to know one *good* textbook thoroughly, and that the college board examinations have, in turn, affected the contents of the more reputable textbooks, and therefore, it is necessary to use one textbook which contains this material. The arguments in favor of more than one book were centered upon the statement that no one author can explain all of the important points, with all their niceties, to every student, and that it is therefore helpful to the student who is puzzled by his classroom textbook to refer to the explanations of another. Further, it is good to help the student to realize that in any serious study of any subject, it is always necessary to refer to more than one source of information. It was also stated that it is not mandatory that any one text be wholly taught, that it might be better to select a few concepts and make sure that these are learned well. Those who desire to utilize other textbooks and reference works but who lack funds for the purchase of these additional books, were reminded that the provisions of the National Defense Education Act provide funds for this purpose; further, the AAAS traveling libraries also provide temporary use of additional books for the use of high school students.

Some conferees suggested that it would suffice to teach a few things well and to this objections were interposed concerning the broad coverage required by the college board examinations. Additionally, it was noted that a knowledge of the process of learning is still largely unknown. It may well happen that, while a teacher is discussing one topic, another topic, discussed earlier, is illumined by the current discussion. Hence, it would not be wise to restrict the treatment of topics to too narrow a field, lest this "accidental" teaching be lost.

Some time was devoted to a discussion of the need to educate students so that they might form an electorate aware of science and its place in contemporary culture. Although the validity of this aim was agreed upon, it also seemed to be the mind of the conference that such an aim could be best met by teaching chemistry as chemistry to the students; there is no reason to overtly emphasize this aspect of the teaching of chemistry.

The preceding topic was also related to the problem of teaching chemistry to the non-college-oriented student. And in this connection the question of training technicians in chemistry was discussed. No definite conclusions were reached, but it was noted that colleges do not attempt to train technicians in chemistry.

The conferees also agreed to the proposition that in addition to other secondary aims, the high school course in chemistry should help students learn how to read to achieve understanding and how to write good English.

Some criticism was directed toward college teachers who state to their freshman classes that they should "forget the chemistry learned in high school." This is obviously bad pedagogy, and, in addition, many teachers who make this kind of statement teach as though their students did have previous instruction in the subject. Perhaps this attitude on the part of some college teachers has arisen from their personal knowledge of inadequate teaching on the part of some high school chemistry teachers. The conference agreed that more teachers of high school chemistry should take advantage of the NBC Continental Classroom course in Modern Chemistry and of the inservice institutes and summer institutes sponsored by the National Science Foundation. It was also pointed out that the high school chemistry teachers were themselves the product of the colleges and that deficiencies in high school chemistry teaching can perhaps best be corrected at the source.

Because of the requirement that every student be exposed to a course in science, classes in high school

[2] YOUNG, JAY A., Prentice-Hall, Inc., 1958.

chemistry often contain students of widely varying abilities. Where possible, such groups should be divided into groups according to their abilities in order to enable the teacher to help each group to the maximum possible degree.

Supporting Role of the Professional Scientist

Several specific ways in which the professional scientist in the community could help the high school teacher were mentioned.

Visiting lecturers to the high school classes. However, the students should be prepared for these lectures by the teacher, and the scientist himself should also be "prepared" by the teacher. In the past, some visiting lecturers have not been as valuable as they could have been due to failure to follow these two precautions. Basically, lecturers are most successful with prepared classes when they communicate to the students some of the "flavor" of their own work in science. Also, the use of *post-mortem* critiques by the teacher with the visitor would be helpful. A list of suggestions to the speaker (prepared beforehand by the teacher) would also be useful. One danger to be avoided is the diversion of the class to another topic by the lecturer. It is desirable that the lecturer supplement the current work in progress, not that he divert the class by speaking on a topic only remotely related to the student's classroom work.

Career counseling by professional scientists to one, or to very small groups of, students was recommended. Counseling on science projects, when possible, was recommended.

The *availability of consultants* for teachers who find that they need additional information in order to help their students was recommended.

These recommendations can be carried out more efficiently if there is first prepared a roster of scientists in the community who are willing to help. This roster should be made available to teachers with listings by topics rather than by alphabetized names of speakers.

An *increase in the availability of summer employment* in chemistry for high school students would be of great help to the students who are interested in chemistry and to their teachers who could then use this new enthusiasm on the part of the student to help the student reach a better understanding of chemistry. In this connection it was mentioned that the American Heart Association program provides for the employment of several high school students in local college and university laboratories for the summer of 1960. Other activities are also available, such as the two-week summer science seminars at Clemson Agricultural College and at other institutions.

Help of Universities. All the conferees agreed that the universities in the area could help by calling other conferences such as this one, with the participants prepared to discuss topics in the same general area. The universities, colleges and industries could help the high school teachers by scheduling regular and frequent seminars in which current developments in specialized fields of chemistry would be discussed. Such seminars should be kept small in terms of numbers of participants.

Conferences a Success

In addition to the conferences outlined above, a similar series was held in each of the disciplines of biology, mathematics and physics. Except for the summarizing conferences, there was little duplication in participants so that approximately 100 different persons attended each discipline or about 400 in all.

Topics for discussion at the various meetings differed somewhat according to the discipline and to the composition of the groups. However, there was one note of universal accord, the beneficial result from a lively discussion in which all have a common interest. As a result of the enthusiastic acceptance of these conferences, it was decided to hold them on an annual basis. Furthermore, it was recommended that they be extended to include a series on the teaching of junior high school science and mathematics. In the latter case, participants would include teachers from the two grade levels, together with scientists from the community. A renewal of the grant from the National Science Foundation to the Washington Academy of Sciences has made it possible to do this.

The success of these conferences held in the Washington area commends this activity for consideration elsewhere. The opportunity for a friendly discussion of academic problems outside of the jurisdiction of a school system provides a mechanism for better mutual understanding of scientific educational matters, serves to delineate problem areas, and focuses attention on methods for their solution.

Statistical Design—Collected Articles

The editors of *Industrial and Engineering Chemistry* have prepared a special reprint booklet of the bimonthly feature "Statistical Design." For six years, 1954–59, Dr. W. J. Youden, whose name is synonomous in the chemical world with his book "Statistical Methods for Chemists," has been the contributing editor for the column.

The increasing awareness among chemists of the importance of experiment design and the efficiency imparted to research by planning in the light of statistical analysis makes the appearance of this volume welcome. The 72-page booklet is offered at $2.00 per copy from: Reprint Department, ACS Applied Publications, 1155 Sixteenth Street, N. W., Washington 6, D. C.

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Method for Attaching Glass Water Aspirators to Water Lines

In our experience, metal water aspirators have not been very successful. They are attacked by corrosive substances and in most instances fail to produce a satisfactory vacuum after a short period of use. By contrast, as illustrated in Figure 1, glass aspirators are fast and efficient, usually rapidly attaining a vacuum approaching the vapor pressure of water. The difficulty of attaching them to the water line is their major drawback. Whereas metal pumps may be screwed into a metal fitting, glass pumps must be attached by a length of compressible tubing clamped to the glass neck of the pump.[1]

We have devised a means of screwing glass aspirators to water lines by means of metal pipe bushings. This method is quick, inexpensive, and effective. Moreover,

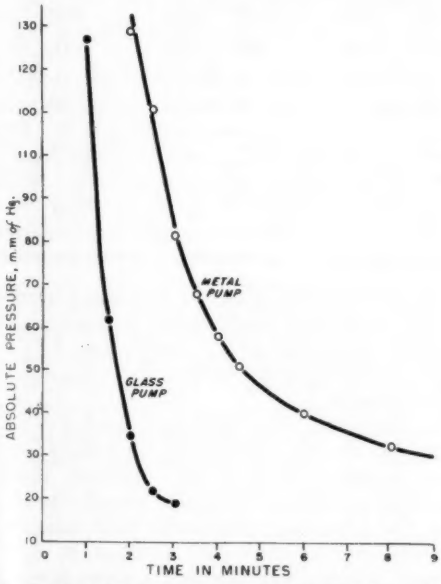

Figure 1. Dynamic test glass versus metal water aspirators. Evacuation time for 5-liter glass flask through 30 in. of $^3/_{16}$-in. bore rubber vacuum tubing.

it has met with the complete approval of our plumbing shops. In the several years since its adoption, we have put dozens of these pumps into service, and have not encountered a single instance of aspirator failure due to breakage or detachment. The method used is illustrated in Figure 2.

The water feed tube of the aspirator[2] is cut off conveniently near the ring seal and replaced by a piece of 9 mm o.d. glass tubing approximately 35 mm long. A $^1/_4$-in. × $^3/_8$-in. (nominal iron pipe size) pipe bushing (hex-nut type, preferably of brass) is bored out to $^1/_2$-in. i.d. This bushing is slipped over the water feed tube of the aspirator to the position shown in Figure 2. The end of the feed tube is then flared to form a strong shoulder approximately $13^1/_2$ mm in diameter. It is absolutely essential that this flare be too large to pass through the bushing, and yet be small enough to pass without interference into the pipe fitting to which the aspirator will be attached. A surprising amount of irregularity is permissible in this flare before untoward results are encountered, but if the flare does not pass easily into the female thread of the pipe line, it will inevitably be broken.

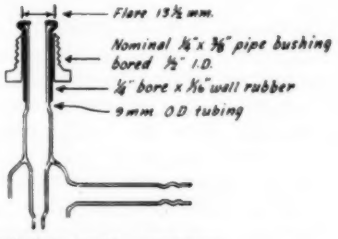

Figure 2. Detail of pipe bushing attachment.

A sleeve of $^1/_4$-in. bore × $^1/_{16}$-in. wall rubber tubing is slipped over the flare, and between the feed tube and the pipe bushing, in such a way that part of the tubing surrounds the flare. Castor oil may be used as a lubricant to facilitate this procedure. The rubber tubing is cut off to a length that will not impede the water flow, and the aspirator is attached to the water line.

In use, a certain amount of leakage between seal and bushing is sometimes encountered, especially when the pump is first turned on. Full water pressure usually suffices to effect a tight seal at this point. We regard a small amount of leakage here as acceptable, since it runs into the drain. Most seals do not show this leakage, and the purist can no doubt eliminate it entirely by carefully making the flare and preparing of the end of the pipe bushing. Since the rubber sleeve cushions the feed tube against the metal bushing, the pump will stand a lateral blow of surprising force without breaking. The pump is free to rotate in the bushing, and the vacuum outlet can be turned to any desired position.

Joint contribution from the Laboratory of Chemistry, National Institute of Arthritis and Metabolic Diseases, and the Rocky Mountain Laboratory, National Institute of Allergy and Infectious Diseases, National Institutes of Health, U. S. Public Health Service, Department of Health, Education, and Welfare, Bethesda 14, Maryland.

[1] The Scientific Glass Apparatus Company offers a large-sized aspirator (Cat. No. J-4965) which utilizes a piece of Pyrex pipe and pipe flange to effect a solid connection to the water line.

[2] Scientific Glass Apparatus Company Cat. No. J-4960, or any similar aspirator may be used.

Proceedings of the

California Association of Chemistry Teachers

Anton B. Burg
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Los Angeles 7

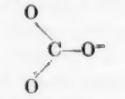
Bonding in Boron Compounds and in Inorganic Polymers

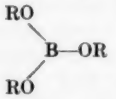
The element boron is such a close neighbor of carbon in the periodic system that one might expect it to offer an equally extensive and varied chemistry of covalent compounds. Such a prospect is on the way toward fulfillment, although long delayed by technical difficulties, the need for a more advanced theory, and the absence of the effective motives which brought thousands of research workers to the study of organic chemistry. The recent increase of interest has led to a great demand for chemists having graduate training in boron chemistry, with a shortage which has been partially met by the adaptation of relatively imaginative organic chemists to this complex subject.

Boron-Carbon Analogies, Planar and Tetrahedral

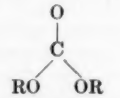
This adaptation has not been unusually difficult, for the route from carbon to boron chemistry can be found through analogies, which must be studied with due regard for important chemical differences between boron and carbon compounds having similar structural patterns. For example, there has been a long history of compounds in which carbon is in the middle of a triangle of other atoms: the carbonates, carboxyl acids, ureids, olefines, and the highly developed class of aromatic compounds. But this plane triangular form is just the classical type for boron: the planar BX_3 pattern, where X can be halogen or one valence of oxygen, sulfur, nitrogen, antimony, or carbon. This carbon-boron analogy is seen clearly in the following structures, in all of which we see either boron or carbon in the plane of three surrounding atoms, some or all of which share out-of-plane electrons for π-bonding to boron or carbon.

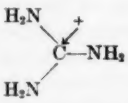
Presented at the Summer Conference on the Teaching of Chemistry, Asilomar, California, August, 1959.

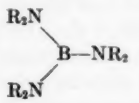

Carbonate

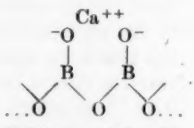

Borate ester

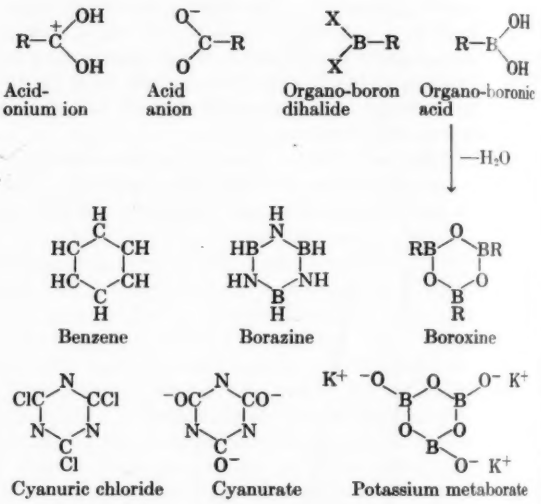
Boron fluoride


Carbonate ester


Guanadinium ion

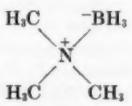

Tris(amino)borine

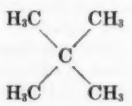

Calcium metaborate

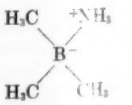


In all of these examples, the π-bonding involves the idea of single-bond:double-bond resonance, or the equivalent molecular orbital description, in the same manner for boron as for carbon, but with some differences of polarity.

Now these and other structural analogies are clear enough, but the BX_3 compounds often show a most important property which is not commonly noticed for the analogous carbon compounds, namely the ability to replace the π-bonding by a dative bond using electrons from some basic molecule such as ammonia or trimethylamine. In this way the boron atom develops tetrahedral bonding and so imitates the great variety of saturated hydrocarbons and their substitution derivatives. The following comparisons of tetrahedral boron, carbon, and nitrogen compounds will serve to show the analogy:


mp 95°
bp est. 171°
Strong B—N bonding
BH_4^- salts
Hydride source


mp −20°
bp 10°
CH_4


mp 56°
bp est. 110°
Unstable B—N bonding
NH_4^+ salts
Proton source

However, this structural analogy between neopentane and the N—B complexes, or between CH_4 and BH_4^- or NH_4^+, must be supplemented by real knowledge of the character of the compounds. The N—B dative bond in $(CH_3)_3NBH_3$ and in $(CH_3)_3BNH_3$ means polarity, so that both compounds are far less volatile and higher-melting than neopentane. Also, if N—H is one of four bonds to N, a proton can be released for acid behavior, whereas if B—H is one of four bonds to boron there is a tendency to release H^- for base-action toward acids. For example, HCl attacks a B—H bond to form H_2 and B—Cl bond—a reaction the like of which is virtually unknown in organic chemistry.

The movement of boron out of the BX_3 plane to make the fourth σ-bond is of course resisted by the strength of the π-bonding, which varies widely over a range of different planar structures. The following periodic-system arrangement of BX_3-planar compounds now can be compared in regard to strength of π-bonding and its relation to the stability of the four-bonded boron complexes.

R_3B	$(R_2N)_3B$	$(RO)_3B$	BF_3
R_2BX	$(R_2N)_2BX$	$(RO)_2BX$	
RBX_2	R_2NBR_2		
...	...	$(RS)_3B$	BCl_3
		$(RS)_2BR$	
		$RSBR_2$	
...	...	Se ?	BBr_3
...	$(CH_3)_2SbBH_2$	Te ?	BI_3

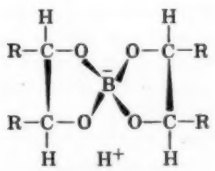
The boron trihalides have relatively weak π-bonding, so that the fourth orbital of boron is not strongly occupied but can offer a low energy level for bonding electrons offered by a base. The π-bonding is strongest in BF_3, but the highly electronegative fluorine atoms claim the major share of the σ-bonding electrons, so that the fourth orbital is very effective for bonding a base to boron, even though some π-bonding must be overcome. In fact, the complexes of BF_3 are generally at least as stable as the corresponding complexes of BCl_3. Such complex-formation is the basis for the widespread use of BF_3 as a catalyst for organic reactions; the boron strongly attracts electrons on the carbon compound, activating it for many reactions in which a carbon atom becomes an electron-acceptor.

Far weaker electron-acceptors are the $(RO)_3B$ compounds in which the π-bonding between oxygen and boron is relatively effective. Much of the energy offered by the formation of a base-to-boron dative bond must be expended to overcome the O-to-B π-bonding, and the resulting tetrahedral complexes usually are not very stable. The case of $(RS)_3B$ compounds is not yet well known and it is difficult to predict whether the poor π-bonding here will permit strong complex-formation, or whether the low electronegativity of sulfur will lead to more electron-density around boron and so a weakening of its acceptor action. There is less doubt in the case of aminoboron compounds such as the $(R_2N)_3B$ type, for the N—B π-bonding here is very strong, and boron is quite unable to attract the electrons of an added base.

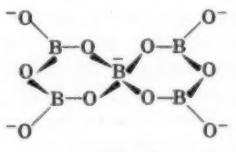
The case of trialkylboron compounds is curious, for one might think that boron has access to only six bonding electrons, so that a fourth bond would form with great strength. However, there are three effects working against strong electron-acceptor action: (1) since carbon is not nearly so electronegative as the halogens, its effective covalence does not leave boron in a strongly electron-attractive situation; (2) the alkyl groups exert some steric interference against the tetrahedral pattern; and (3) the C—H bonding electrons have some action toward π-bonding to boron. This use of C—H bonding electrons to make other bonds may seem strange to the classical organic chemist, to whom a bond is a pair of electrons between two atoms, but such a delocalization of bonding electrons is taken in stride by modern theorists. The principle is fairly simple and widely applicable: a pair of electrons normally assigned to a specific bond can visit any neighboring atom which offers an energetic empty orbital pointing in the right direction; and the deeper the energy level of such an orbital, the stabler the compound will be. Stability also is improved if the electron-pair visits more atoms in this way. Much of the discussion of ordinary and hyperconjugative resonance is merely a recognition of this main principle of electronic delocalization.

The same ideas can be applied to the enormous variety of BX_2Y and BXYZ compounds, whose behavior toward bases depends upon the electronic behavior and steric effects of the X, Y, and Z groups, each differently affecting the action of the others. Thus the stability of the boron complexes has a very intricate theoretical basis but is important on account of the bearing which it has upon a fairly wide variety of reaction mechanisms in organic chemistry.

A biologically important example of the boron tetrahedron is presented by the spiranes which boric acid forms by reaction with many cis-diols such as glycerol, mannitol, and various sugars. The tendency toward a stable planar BO_3 pattern makes such com-



Boro-spirane



Anion of $K(H_3O)_2H_2B_5O_{10}$

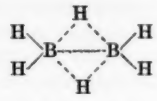
In each case the two rings are in mutually perpendicular planes.

plexes unstable, but the displacement of a hydrogen ion in forming a spirane from boric acid makes a quantitative titration feasible. The formation and dissociation of such spiranes probably are involved in the process of conversion of sugars to starch and cellulose in plants, so that very small traces of boric acid are necessary and sufficient for promotion of vegetable growth. Accordingly it has become standard practice to use some form of boron oxide in fertilizers for boron-deficient soils. A commonly used form is potassium pentaborate, the spirane structure of which is here shown.

Diborane and the Polyboranes

The boron hydrides represent an extreme departure of boron from analogies to carbon, for even the simplest case, the gaseous substance known as diborane (B_2H_6), has a type of bonding quite alien to the usual organic-chemical ideas of valence. It is clear that a BH_3 group

cannot be a stable molecule because the boron would have an energetic empty valence orbital. Hence a substance composed only of BH_3 groups would have to associate in some way to permit a greater sharing of electrons. This can be accomplished by forming a square $B\begin{smallmatrix}H\\H\end{smallmatrix}B$ pattern in which two pairs of electrons form one B—B bond and four B—H bonds, and each of these five bonds has about half the strength of a single bond. Thus each boron atom has approximately

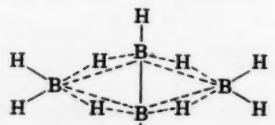


Diborane (bp −93°)

the tetrahedral pattern of carbon in methane but still may be said to be bonded to five neighboring atoms—four hydrogen and one boron.

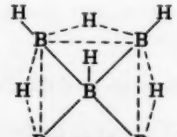
This structure still is not the stablest combination of boron with hydrogen, for diborane decomposes slowly at ordinary temperatures, forming first small proportions of the even less stable tetraborane-10 and pentaborane-11 by reactions which are reversed by the presence of hydrogen. Heating this equilibrium system leads to the far stabler pentaborane-9 and decaborane-14. The very rare boron hydride hexaborane-10 can be made from the unstable tetraborane-10 or pentaborane-11; and there is evidence for the existence of boron hydrides having seven, eight, and especially nine boron atoms per molecule. But the final stages of stabilization of a boron-hydride system are found in the non-volatile polymers, having empirical formulas such as (BH)x. The whole trend of decomposition thus is toward highly condensed structures having less and less hydrogen per boron and with an increasing complexity of poly-center bonding. The following display of structures shows this general trend toward the more stable highly condensed patterns (*1*).

These flat patterns actually represent three-dimensional structures, such that the boron atoms usually could be placed on the surface of a sphere, with the hydrogen atoms all extending outward. Such a sphere would be only about 20% covered by B_4H_{10} but about 80% covered by $B_{10}H_{14}$. The three-center B—H—B electron-pair bonds are shown by dotted lines, and various BBB triangles also could be designated as three-center bonds. The rule is that there are just as many three-center bonds as boron atoms. Thus every boron atom has more than four near neighbors (either boron or hydrogen); yet no boron shares more than an octet of electrons, nor any hydrogen more than one pair.



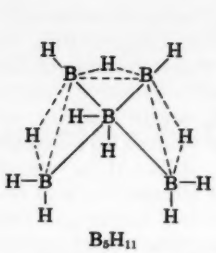
B_4H_{10}

mp −120°; bp +17°



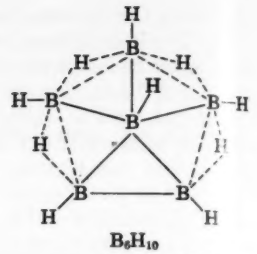
B_5H_9

mp −47°; bp +48°



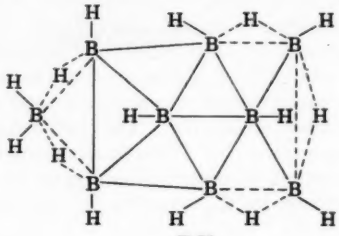
B_5H_{11}

mp −123°; bp −63°



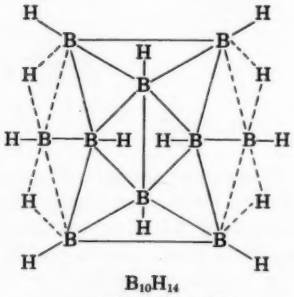
B_6H_{10}

mp −65°; bp 120°



B_9H_{15}

mp −20°



$B_{10}H_{14}$

mp 100°; bp 210°

The Boron Hydrides as Electron-Acceptors: Borine Complexes

All of these boron hydrides might be said to be electron-deficient, for bond-strength can be gained by bringing in electrons to break down the three-center bonds and form classical two-center bonds. Even in the relatively simple case of diborane there are several ways to accomplish this. One can add sodium to an ether solution of diborane, which takes electrons and disproportionates into salts of the BH_4^- and $B_3H_8^-$ ions (*2*). Another unsymmetrical break-down occurs in the unusual reaction of diborane with solid ammonia, to form the salt $(NH_3)_2BH_2^+BH_4^-$ (*3*), leading to still more complicated behavior in liquid ammonia. Or one can pass diborane into a saturated solution of sodium in liquid ammonia to form salts of a nature yet to be clarified.

But the best-known type of diborane reaction is the formation of complexes such as $(CH_3)_3NBH_3$. Here there is a symmetrical cleavage of the bridge bonding, so that boron has its valence electron-octet without resort to three-center bonding. Also most of the higher boranes can form BH_3 complexes, as might be expected if we note that their structures contain BH_3 groups held only by bridge or three-center bonds. In such cases the remainder of the polyborane molecule also receives the base, and often obtains a highly polymeric resin in which the base is entrapped and exerts a

Table 1. Borine Complexes of the Non-rearranging Type

Formula	Volatility (P_{mm}/°C)	Vapor-phase dissociation
$(CH_3)_2O \cdot BH_3$	18 mm/−78°	Near 100%
$(CH_3)_2O \cdot BD_3$	32 mm/−78°	Near 100%
$(CH_3)_2S \cdot BH_3$	4.3 mm/0°	60% at 53°
$(CH_3)_3N \cdot BH_3$	1 mm/27°	Nil at 200°
$C_5H_5N \cdot BH_3$	1.8 mm/100°	Nil at 200°
$(CH_3)_3P \cdot BH_3$	3 mm/50°	Slight, above 200°
$(CH_3)_3As \cdot BH_3$	7 mm/47°	Slight at 120°
$(CH_3)_3Sb \cdot BH_3$	exists?	Complete
BH_3CO	320 mm/−78°	Extensive
BH_3PF_3	267 mm/−80°	Extensive; may decompose to solids
$LiCH_3 \cdot BH_3$	Involatile salt	.....
$LiH \cdot BH_3$	Involatile salt	.....

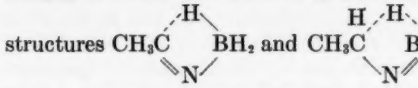
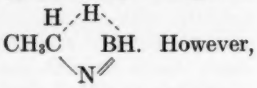
stabilizing influence. The removal of the BH_3 group is easiest for the least stable polyboranes, such as B_2H_6, B_4H_{10}, and B_5H_{11}. For the very stable B_9H_9 a very strong base and elevated temperatures are required and for the even stabler $B_{10}H_{14}$ another type of reaction seems to be more feasible.

The energy required to cleave diborane into two BH_3 groups has been estimated as $\Delta H = 28.5$ kcal/mole (*4*). Thus a BH_3 complex can form even if the base-boron bond energy is only about 15 kcal. Accordingly, even fairly weak bases can split diborane rapidly at low temperatures, leading to a wide variety of borine complexes. These may be divided into three main classes: those which cannot easily undergo rearrangements or self-reactions; those which transfer hydride internally to make new products; and those in which the base carries a proton whose acidity is enhanced by the complex-formation, so that a proton-hydride reaction is possible. Tables 1, 2, and 3 show examples of these three types, along with some of their reaction products. The size of the subject can be appreciated by considering that the indicated bases are only prototypes of many classes, and that halogen, oxygen, sulfur, alkyl, or aryl substitution-derivatives of the BH_3 group also form complexes with bases.

Table 1 shows the expected trend toward greater stability with increasing base-strength, and we can even include methide and hydride among the very strong bases which make stable borine complexes. Quite exceptional are BH_3CO and BH_3PF_3 (*5*), which seem to be quite lacking in the polarity effect which renders the other borine complexes far less volatile. If carbon monoxide acts as an electron donor to make a C—B bond, polarity must be expected unless there is some compensating electronic effect. Such an effect could be a drift of B—H bonding electrons into a 2*p* orbital of carbon—as is possible because oxygen has no great tendency to form a triple bond to carbon. Indeed, such a use of the B—H bonding electrons is indicated by the 114° HBH bond angle in BH_3CO (*6*), as though the B—H bonds were pulled apart from the expected 109.5° angle on account of the movement of electrons toward carbon.

Table 2. Borine Complexes Capable of Internal Hydride-Transfer

Formula	Volatility	Further reaction
$(CH_3)_2CO \cdot BH_3$	Unknown	Forms $(i\text{-}PrO)_3BH$ at −78°
$CH_3CN \cdot BH_3$	Slight/25°	Dissociates *in vacuo* or forms ring $(EtNBH)_3$ at 100°
$(CH_3)_2N{-}P(CH_3)_2$ $\quad\quad\quad

hydride-transfer from boron to carbon. The analogous nitrile reaction is far slower, so that the intermediate borine complex can be directly recognized. Here the formation of a CH_3CH_2NBH polymer-unit requires the transfer of two H^- from B to C, presumably through the structures  and  . However, it is not easy to explain why these successive steps require so much more time than is needed for the R_2CO reductions.

The double-base complexes shown in Table 2 are all stable at room temperature but react in a very complicated manner on heating above 100°. In each case there is a bond-rupture between the two basic atoms (N and P or P and P), but the way this happens is quite obscure. For example in the pure substance $(CH_3)_2NP(CH_3)_2 \cdot BH_3$ we are fairly sure that the BH_3 group is attached to P, for CH_3 attaches to P when we form the methiodide $(CH_3)_2NP(CH_3)_2 \cdot CH_3I$ (*7*). Then a simple transfer of hydrogen from boron to nitrogen would give only $(CH_3)_2NH$ and the $(CH_3)_2PBH_2$ polymers. But these polymers are strictly inert toward amines as well as toward many other basic or acidic reagents, so that this simple mechanism could not account for the observed good yields of $(CH_3)_2PH$, $P_2(CH_3)_4$, and the aminoboron hydrides. But we should not attempt to understand these complicated reactions without a fuller knowledge of the aminoborines and phosphinoborines. These are obtained most simply by heating some of the protic-base borine complexes shown in Table 3.

Table 3. Borine Complexes of Bases Having Available Protons

Formula	Dissociation	Forms H_2 at	Products
$H_2O \cdot BH_3$	Extreme; known only by kinetics	−78° and lower	$HOBH_2$ and on to boric acid
$CH_3OH \cdot BH_3$	Extreme; not proved to exist	−78°, etc.	$(CH_3OBH_2)_x$ and on to $(CH_3O)_2BH$ and $(CH_3O)_3B$
$H_3N \cdot BH_3$	Nil	30°	$(HNBH)_3$, etc.
$CH_3NH_2 \cdot BH_3$	Nil	30°	$(CH_3NBH)_3$ only
$(CH_3)_2NH \cdot BH_3$	Nil	30°	$(CH_3)_2NBH_2$, etc.
$CH_3SH \cdot BH_3$	Appreciable at −78°	−78°	$(CH_3SBH_2)_n$
$H_3P \cdot BH_3$	200 mm at 0°	65°	$(BPH_{3.75})_x$ condensed polymer
$CH_3PH_2 \cdot BH_3$	Slight at 85°	100°	$(CH_3PHBH_2)_x$ high polymer
$(CH_3)_2PH \cdot BH_3$	Nil	150°	$(CH_3)_2PBH_2$ trimer, tetramer, etc.
$CH_3AsH_2 \cdot BH_3$	10 mm at −78°	25°	$(CH_3AsHBH_2)_x$, losing H_2 to form cross-links
$(CH_3)_2AsH \cdot BH_3$	8 mm at 0°	50°	$(CH_3)_2AsBH_2$ trimer, tetramer, etc.
$(CH_3)_2SbH \cdot BH_3$	(Existence uncertain, −78°)	−60°	$(CH_3)_2SbBH_2$ monomer only

In all of these borine complexes the principle of further reaction is an attack by protons upon the hydridic B—H bond, such that (Base-H)·BH_3 forms H_2 and Base-BH_2 units. It seems that the formation of any polar BH_3 complex greatly enhances the hydridic character of the B—H bond, regardless of the strength or weakness of the base, for HCl attacks all of them at low temperatures to form hydrogen almost as rapidly from the weak-base complexes as from the strong-base complexes (*8*). Hence the great differences in the rates of the hydrogen-forming self-reactions of these borine complexes cannot be ascribed to differences of hydridic character, but must be attributed to differences of proton activity. We must suppose that the formation of the base-boron dative bond makes it easier to remove H^+ from the base atom. For example the hydrolysis of diborane probably begins with a very fast formation of the complex $H_2O \cdot BH_3$, in which the H—O bond should be about as labile as in H_3O^+. This lability would explain why diborane hydrolyzes so very rapidly. On the other hand, the N—H bond in $H_3N \cdot BH_3$ should be only about as acidic as the NH_4^+ ion, so that the complex loses hydrogen only very slowly at room temperature. Obviously the protic-acid character of the complex varies inversely with the strength of the base, so that the BH_3 complexes of weaker protic bases are both easier to dissociate into base and diborane, and more easily caused to form hydrogen. This principle is evident from the data in the middle columns of Table 3.

Table 4. N—B Analogues of C—C Compounds

Substance	Carbon analogue	Polymeric character
$(H_2NBH_2)_x$	Polyethylene	Monomer unknown; loses H_2 easily
$(CH_3NHBH_2)_3$	1,3,5-Trimethylcyclohexane	Monomer unknown
$(CH_3)_2NBH_2$	2-Methylpropene	Rapidly reaches a monomer-dimer equilibrium favoring dimer
$[(CH_3)_2NBH_2]_3$	1,3,5-Hexamethyl cyclohexane	Forms from preceding, by reaction with B_2H_6; stable trimer
$H_2NB(CH_3)_2$	2-Methylpropene	Polymerizes reversibly
$(CH_3)_2NBHCH_3$	2-Methylbutene-2	Slowly reaches a monomer-dimer equilibrium favoring monomer
$CH_3HNB(CH_3)_2$	2-Methylbutene-2	Associated form occurs in liquid, especially at low temperatures
$(CH_3)_2NB(CH_3)_2$	Tetramethylethylene	Monomer only; mp −92°; bp 65°
$(HNBH)_3$	Benzene	Ring with π-electrons nearer to N than to B; bp 53°; condenses on standing, forming polymer + H_2
$(CH_3NBH)_3$	Mesitylene	Permanently stable; bp 134°
$(HNBCH_3)_3$	Mesitylene	Permanently stable; bp 129°
$(CH_3NBCH_3)_3$	Mellithene	Stable; m.p. 97°; bp est. 227°
Planar $(BN)_x$	Graphite	White, soft insulator; infinite hexagonal planes layered differently from graphite
Tetrahedral $(BN)_x$	Diamond	Hard as diamond, and stable to higher temperatures in air

Aminoboron Hydrides

Just as we have seen that R_3NBH_3 complexes are formally analogous to hydrocarbons (by substituting N—B for C—C) we can also find N—B compounds that are analogous to olefines and their polymers, to

aromatics, and to both forms of pure carbon. The following examples (Table 4) illustrate such analogies, which are best viewed with the intention to find sharply different properties.

The polyethylene analogue $(H_2NBH_2)_x$ forms cross-links very easily, with spontaneous loss of hydrogen so that if one heats it the trend is toward the HNBH high polymers and eventually boron nitride. The tendency to form a high polymer decreases with increasing methylation either on boron or on nitrogen, although this rule may be modified when more is known of the new type of reaction which occurs when $(CH_3)_2NBH_2$ reacts with B_5H_9 to form the ring trimer $[(CH_3)_2NBH_2]_3$. All of these olefine-like monomers readily employ the nitrogen atom for base-action toward strong electron-acceptors, or the boron atom for Lewis-acid action toward bases—reactions which are far more difficult for the electronically more symmetrical olefines. Similarly, the aromatic-type $(BN)_3$ ring compounds have far more base-character than the organic aromatics, and also a Lewis-acid character well beyond the slight electron-attracting character of benzene. Accordingly it is not surprising that borazine, $(HNBH)_3$, can associate with molecules of its own kind, building up a high polymer by N—B bonding with loss of hydrogen. This tendency is less for the organic derivatives of borazine.

Also interesting is the contrast between boron nitride and graphite. Both form parallel planes of hexagonal rings, but BN has none of the metal-like properties which we associate with the delocalized π-electrons in graphite. Evidently the similar π-electrons in BN are more localized on N than on B and do not travel so well through the inter-layer regions. But any sharing of these π-electrons between N and B would mean polarity, and so we find that each N atom is in the middle of a vertical line connecting two B atoms in the two adjacent planes—whereas each graphite plane has half of its C atoms on lines through the ring-centers in the adjacent planes.

More nearly similar are borazon and diamond, in both of which all atoms are tetrahedrally bonded. In borazon, of course, we must recognize some polarity in the B—N bonding, and this may help to account for the higher thermal stability of borazon (*9*).

The Aminodiboranes

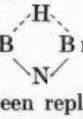
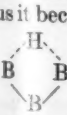
Sharply deviant from the carbon analogies are the aminodiboranes, $R_2NB_2H_5$, which have the  ring; one bridging hydrogen in diborane has been replaced by the R_2N group. When this structure was proved by electron diffraction, it became clear for the first time that one BHB three-center electron-pair bond could occur without another one parallel to it as in diborane. Thus it became easier to believe the X-ray results showing  rings in the higher polyboranes; for example B_5H_9 has four of them. Examples of the aminodiboranes are shown in Table 5.

Table 5. Examples of the Aminodiboranes

Formula	Volatility (P_{mm} at t°C.)	Manner of decomposition
$H_2NB_2H_5$	32/0°	At room temperature, forms B_2H_6 and the strongly-bonded polymer $(H_2NBH_2)_x$, which condenses further
$CH_3NHB_2H_5$	48/0°	Loses diborane reversibly, forming $(CH_3NHBH_2)_x$—probably trimer
$C_2H_5NHB_2H_5$	19/0°	Similar to the above
$C_3H_7NHB_2H_5$	11/0°	Similar to the above
$(CH_3)_2NB_2H_5$	101/0°	Stable at elevated temperatures: forms B_2H_6 and $(CH_3)_2NBH_2$ in low-pressure stream at 350°
$C_3H_6NB_2H_5$	6/0°	Dissociates to B_2H_6 and polymeric $C_3H_6NBH_2$
$C_4H_8NB_2H_5$	22/27°	Like $(CH_3)_2NB_2H_5$
$C_5H_{10}NB_2H_5$	7.6/25°	Like $(CH_3)_2NB_2H_5$
$CH_3NSiH_2B_2H_5$	81/0°	Dissociates at room temperature to B_2H_6 and monomer $CH_3NSiH_2BH_2$, and beyond
$(SiH_3)_2NB_2H_5$	74/0°	Like the above, but less stable

The stabler members of this class are easily made just by heating an aminoborine with diborane. For less stable aminodiboranes, one must use more delicate methods, as in the case of $H_2NB_2H_5$. To obtain this, one heats the compound $B_2H_6 \cdot 2NH_3$ in a stream of diborane and captures the unstable product in a trap cooled by liquid nitrogen. What makes it unstable is the loss of energy when the polymer $(H_2NBH_2)_x$ is formed from it—whereas $(CH_3)_2NB_2H_5$ is relatively stable (*10*) because it can only dissociate to B_2H_6 and $(CH_3)_2NBH_2$, with no important evolution of polymer bonding energy. The situation is intermediate for $CH_3NHB_2H_5$, the dissociation of which gives the moderately well-bonded polymeric CH_3NHBH_2.

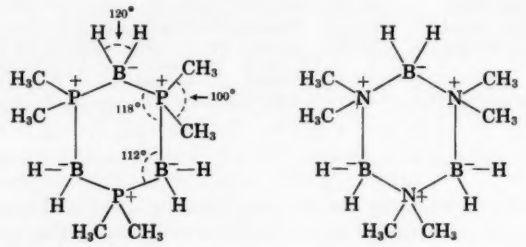
In the ring-aminodiboranes made from azetidine, pyrrolidine, and piperidine, we find an effect of bond-strain on instability (*11*). When the N atom is part of a ring of five or six atoms the situation is much like that in $(CH_3)_2NB_2H_5$, where the only strain on the nitrogen bonding is in the 76° BNB angle. But when nitrogen must also form a 90° angle between bonds to carbon, in a C_2N ring, another situation is stabler and the aminodiborane $C_3H_6NB_2H_5$ breaks down to release diborane and form a glassy polymeric $C_3H_6NBH_2$. Even more strain is found in the C_2N ring of ethylenimine, so that it is not possible even to make any of the corresponding aminodiborane, $C_2H_4NB_2H_5$ at all. Instead, the ring opens and hydrogen goes from boron to carbon, so that we obtain ethylaminodiborane, $C_2H_5NHB_2H_5$. This is one more example of an internal hydride-shift, beginning with a BH_3 complex.

In the silylaminodiboranes instability has yet another cause: the lack of nitrogen base-strength when SiH_3 groups are attached to N. For example, $(SiH_3)_3N$ has an equilateral triangle of Si atoms with N at the center (*12*), using its lone-pair electrons for a three-way π-bond to the 3*d* orbitals of Si—and thus the base-action is so poor that this tertiary amine fails to make a BH_3 complex. A similar effect in $(SiH_3)_2NBH_2$ favors a planar form in contrast to the tetrahedral nitrogen in $(SiH_3)_2NB_2H_5$, which can be formed from $(SiH_3)_2NBH_2$ only under several atmospheres pressure of diborane, and easily dissociates at lower pressures (*13*). The monomeric $(SiH_3)_2NBH_2$ itself is unstable, forming first a dimer by an irreversible process

which leads further to SiH_4 and a plastic material which is not likely to have industrial interest because it catches fire on exposure to air.

Polymers of the $(R_2PBH_2)_n$ Type

Unlike $(CH_3)_2NBH_2$, the $(CH_3)_2PBH_2$ unit never forms a monomer; indeed we never could make a $(CH_3)_2PB_2H_5$ because the $[(CH_3)_2PBH_2]_n$ polymers are far too stable. Of these, the smallest, stablest, and least reactive is the trimer, whose structural pattern is compared with the stable $[(CH_3)_2NBH_2]_3$ as follows (*14*, *15*):



These patterns have the chair shape of a hexamethylcyclohexane, but one difference is the electron-dative character of the ring bonding, such that each boron atom has a formal negative charge and each phosphorus a formal positive charge. Thus B repels B and P repels P, and this must be one reason that the $(PB)_3$ ring is flatter and has wider angles than the cyclohexane analogue. How important this effect may be, may be judged after the ring angles in the aminoborine trimer have been determined.

Of these two ring compounds $[(CH_3)_2PBH_2]_3$ seems to be the more resistant to decomposition by heat, and less reactive to acidic or basic reagents which might be expected to break down such dative-bonded rings. It actually resists concentrated hydrochloric acid up to 300°, and is not appreciably decomposed by heat alone even at somewhat higher temperatures. It is stable in the open air up to 180°, and is only partially attacked during months with sodium and sodium amide in liquid ammonia under pressure at room temperature. Such extreme stability and chemical resistance would be quite surprising in terms of conventional ideas, for phosphorus bases usually are weaker than their nitrogen analogues, so that a dative-bonded $(PB)_3$ ring would be easier to disrupt than its $(NB)_3$ analogue. But there is one kind of electronic behavior that is possible for phosphorus but not for nitrogen: the use of *3d* orbitals for interaction with electrons from neighboring atoms. Thus we may consider a kind of three-center π-bonding effect whereby the B—H bonding electrons belong also partially to phosphorus. Such an effect would stabilize the $(PB)_3$ ring not only by the extra bonding itself, but also because it would tend toward neutralizing the formal charges associated with the direct P—B dative bonding. It would also explain why the HBH angle can be as wide as 120°.

The same kind of delocalization of B—H bonding electrons seems necessary to explain why the compound $[(CF_3)_2PBH_2]_x$ can be heated to 200° without immediate decomposition, even though the two very electronegative CF_3 groups on P make it a very poor electron donor—such as would never hold the ring together by P—B dative bonding alone. Indeed, such electronegativity would greatly improve the power of the *3d* orbitals to attract the B—H electrons, so that the supplementary bonding may well be a major reason that the compound is stable.

Another example of this general type of polymer bonding is offered by the corresponding arsenic compounds, $(R_2AsBH_2)_n$. These are just like the phosphinoborines except that they are not so stable. The following comparisons are pertinent (*16*, *17*):

$[(CH_3)_2PBH_2]_3$ stable and even formed from the tetramer at 350°. Hydrolysis at 300–325° gives $12H_2$ and $3(CH_3)_2POOH$ but no methane.	$[(CH_3)_2AsBH_2]_3$ forms from the tetramer at 180°; decomposes at 200°. Hydrolysis at 200° gives much methane, some 5-valent As, and some $(CH_3)_2AsH$.
$[(CH_3)_2PBH_2]_4$ stable at 255°, decomposing at 350°; good hydrolysis at 300° to $16H_2$ and $4(CH_3)_2POOH$.	$[(CH_3)_2AsBH_2]_4$ decomposes at 180° to make some trimer.
$[(CH_3)_2PBH_2]_x$, formed in very small yield, goes to trimer at 173°.	$[(CH_3)_2AsBH_2]_x$ formed in moderate yield, easily converted to trimer and tetramer.

Even less stable and more reactive than the arsinoborines are the low polymers of the CH_3SBH_2 unit, which result when the unstable complex $CH_3SH{\cdot}BH_3$ loses hydrogen during a slow warming from −78° (*18*). Their easy interconversion has prevented isolation of specific members of the class, such as the trimer or the tetramer. Presumably the S—B dative bonding between the CH_3SBH_2 units is not very strong; and indeed it is easily broken by using a strong electron donor such as trimethylamine. Then the monomer complex

$$(CH_3)_3N:B(H)H:S(H):CH_3$$

easily reacts with a stream of diborane to make the unstable $CH_3SB_2H_5$. At room temperature, this reverts rapidly to $(CH_3SBH_2)_n$ and diborane.

The phosphinoborine-arsinoborine comparison can be extended one element farther down the fifth group, to the $(CH_3)_2SbBH_2$ unit (*19*). This is known only as a monomer, as one might expect by knowing what a weak electron-donor the $(CH_3)_2Sb$ group must be. On that basis alone, however, one might expect $(CH_3)_2SbBH_2$ to have a very active boron atom, capable either of holding a base such as trimethylamine or of forming a diborane-type bridge to make a dimer of the known $(RBH_2)_2$ type. Actually, however, it does neither: it does not associate, is stable up to 200°, and forms no complex with trimethylamine. Thus it seems necessary to assume that the lone-pair electrons on antimony are well shared with boron internally, by some kind of π-bond. This can occur most easily by means of a hybrid, or combination type of orbital, using the antimony *5p* for its low energy level and the antimony *5d* for its effect in extending the electrons toward boron. Such a combination is possible because the antimony *5d* is not far shallower than the *5p*, in regard to energy value.

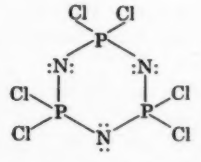
Inorganic Polymers

Throughout this talk we have had occasion to notice various kinds of polymers involving boron with base-forming elements such as nitrogen or phosphorus.

We might now consider some ideas applying to inorganic polymers more generally. One principle of first importance is the tendency of long chains to break down into relatively small rings. It was mentioned that this happens to the higher polymers of the $(CH_3)_2PBH_2$ and $(CH_3)_2AsBH_2$ units, and surely the trimer of $(CH_3)_2NBH_2$ is far stabler than another form purporting to be a long chain of the same units (*20*). This tendency has a definite thermodynamic basis, for the entropy of a system is greater if it consists of many small molecules instead of a few large molecules made of the same amount of material. Hence for the change $n(\text{unit}) \rightarrow (\text{unit})_n$, ΔS is negative and larger per unit when n is bigger. Then the well-known equation $\Delta F = \Delta H - T\Delta S$ means that ΔF is nearer to being positive, and hence less favorable, for the formation of long chains than small rings. For the usual organic polymer, this effect usually is not troublesome at temperatures short of the range where decomposition is more extensive than a mere change to small rings—for the required C—C bond cleavage requires a high energy of activation. For many inorganic polymers, however, such a reorganization is fairly easy and happens at relatively moderate temperatures.

Thus if we want to make a practical plastic based upon an inorganic polymer skeleton and achieve some degree of thermal stability, we must find some effect which will overcome the preference for small rings. One idea is to develop cross-links between the chains, so that if the chains tend to break down into rings, there still is bonding between the rings to make a chain effect, with considerable steric hindrance to the process of breaking down the chains of rings to form rings of rings. However, a more fundamental principle applies if we can select a type of bonding such that small rings would be seriously strained. A good example of this is the nitrilophosphoric chloride system, $(NPCl_2)_n$.

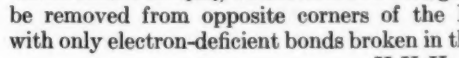
It has been known for more than one hundred years that a whole series of materials all having the empirical formula $NPCl_2$ can be made by the reaction between PCl_5 and NH_4Cl; and in more recent times there has been enough structural research to show that these all are rings or chains in which phosphorus and nitrogen atoms alternate. Now if we consider the following plane-ring structure which is known for the trimer, we find a problem in regard to the disposal of the lone-pair electrons of nitrogen.



In the picture as shown, the formally pentavalent phosphorus would have a positive charge and nitrogen a negative charge. This charge separation would be overcome by allowing some of the nitrogen lone-pair electrons to intereact with the phosphorus 3*d* orbitals. But this effect would be best for the over-all bonding if both lone-pairs on each nitrogen could interact with both adjacent phosphorus atoms; and evidence that this happens is found in the fact that a very strong electron-acceptor, boron trifluoride, fails to attach itself to nitrogen in such compounds. But for this double use of the nitrogen lone-pairs it would be best for the P—N—P bonding to be linear, as could happen in long chains or much larger rings. And sure enough, the $NPCl_2$ system is one in which it is possible to convert small rings to high polymers by heating.

This $NPCl_2$ system bears a certain analogy to the silicones, or we might consider the still more closely analogous $(CH_3)_2PN$ polymers, which have been made very recently (*21*). If we simply use Si instead of P, and O instead of N, it is easy to recognize that we have the same number of electrons, and similar elements, in the well-known $(CH_3)_2SiO$ polymers. In these, it seems that there is much use of the oxygen lone-pairs for bonding via the 3*d* orbitals of silicon, so that the Si—O—Si bond angle is far wider than the tetrahedral 109°, and long chains can be stable relative to the trimer ring. A wide oxygen angle (about 140°) is found also in quartz and the polysilicates, wherein large silicon-oxygen rings are typical.

Another type of polymer, possibly unique to boron, was indicated in relation to the formation of BH_3 complexes from the higher polyboranes. Considering the structure of B_5H_9, we see that two BH_3 groups could be removed from opposite corners of the B_4 square, with only electron-deficient bonds broken in the process.



Then what would be left would be a B:B:B: fragment, with four empty boron valence orbitals and one lone-pair of electrons. Such a unit never could exist as such, but would form instead an infinite polyborane-polymer structure with bonding something like the $B_{10}H_{14}$ pattern. Just such polymeric web patterns, with much three-center BHB and BBB bonding, would account for the many occurrences of materials approximating the $(BH)_x$ composition, as products of moderate-temperature decomposition of polyboranes. But when such a polymer is made by using an amine or phosphine base to remove BH_3 groups from a structure such as B_5H_9, the resulting $(BH)_x$ material includes a molecule of the base for every four or five BH units (*22*). Indeed, the base is so firmly incorporated in the polymer that there is no way to remove it; Lewis acids cannot reach it and heat has no effect except to decompose the base, leaving the base-forming element still in the polymer. The chemical function of this base, of course, is to form an electron-dative bond to boron in the polymer, and this relieves some of the boron from the necessity of forming three-center bonds. The effect is to make a stabler polymer, and indeed it has been possible in this way to make resinous materials which become more and more stabilized as heat drives out small proportions of hydrogen—until the decomposition of the base acts as a limiting factor. With phosphine bases, it has been possible to make transparent resins of approximate type-formula $B_9H_5(\text{Base})_2$, which remain stable indefinitely at 450°. Even with oxygen at such a temperature, such resins are only superficially attacked.

Summary

The foregoing discussion will serve as an introduction to boron chemistry, with special reference to its place

in the wide field of polymer chemistry. It has been possible to give only a sampling of the numerous subtle ideas whereby this kind of chemistry can be understood, and only a few hints of the enormously many unsolved problems and distinct patterns for further research. It would be pleasant to describe the details of this field at far greater length, but there is a limit beyond which the subject might indeed become boron in another sense and spelling. Hence I can only leave the reader to pursue in his own way the further study of any aspect which may seem especially interesting. The following bibliography gives two fairly general sources of further knowledge of boron hydrides and some specific references to recent results not covered by most of the advanced books on inorganic chemistry.

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Chem Ed

LETTERS

To the Editor:

The following mnemonic has been found to be useful in helping students to establish the electron configurations of atoms in the ground state: (See also Simmons, L. M., this Journal, **25**, 698 (1948)).

1,2	2,3	3,4	3,4,5	4,5,6	4,5,6,7	5,6,7,8

The sequence of doublets, triplets and quadruplets thus arranged stands for the order in which *s*, *p*, *d* and *f* orbitals are filled for each main energy level. The first appearance of the number in the sequence stands for *s* orbitals which can accommodate 2 electrons, the second appearance for *p* orbitals which will take 6, the third for *d* orbitals (10 electrons), and the fourth for *f* orbitals capable of holding 14; for example:

1, 2	2,3	3,4	3,4,5	4,5,6	4

Na (11) $1s^2$, $2s^2$, $2p^6$, $3s^1$

Nd (60) $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^2$, $3d^{10}$, $4p^6$, $5s^2$, $4d^{10}$, $5p^6$, $6s^2$, $4f^4$

Moddie D. Taylor

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To the Editor:

Dr. Morgan's excellent magnet-connected polymer models [J. Chem. Educ., **37**, 206 (1960)] reminded me that no note has appeared regarding the availability of large snap-together polyethylene beads. The idea was derived from Blackwell [J. Chem. Educ., **34**, 500 (1957)] and the hollow balls, eggs, and cylinders were found to be available in gross lots from Fisher-Price Toys of East Aurora, Erie County, New York, at seven to eight dollars per gross. The light colors of red, yellow, orange, and light blue are the most easily seen. Purple, dark blue, and green are available. Because the balls are about an inch in diameter, and the other shapes about two inches long and an inch thick, the snapped-together chains are big enough for lecture demonstrations to a group of 200. We have found them very useful in the past two years for organic chemistry and non-technical classes.

Admittedly, the automatic-magnetic-connecting feature of Morgan's models is lacking in the pop-beads, but they are quite useful in demonstrating simple polymerization (e.g., polystyrene is amusingly represented by a chain of cylinders with balls attached to them as the phenyl groups), copolymerization and cross-linked polymers. A third "reactive site," in addition to the two ends of the beads, can readily be made by drilling with a sharp cork borer.

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Occidental College
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Report of the New England Association of Chemistry Teachers

Roger E. Beyler[1]
Southern Illinois University
Carbondale

Some Recent Advances in the Field of Steroids

The very early beginning of steroid research was nearly 150 years ago. At that time European investigators isolated cholesterol and bile acids from the nonsaponifiable lipid fractions of animals. However, very little progress was made in the field until after the structural theory of organic chemistry was firmly established in the latter half of the nineteenth century. Thus the second phase of research in steroids began about 1900. It was characterized by the classical investigations of Windaus on the structure of cholesterol and the bile acids, culminating in final structure proofs in the period 1928–32.

Research: 1930-1955

The next phase of steriod research was in the decade from 1930–40. This depression era may be characterized as "the golden decade" of isolation and structure proof of the steroid hormones. Estrone, testosterone, and progesterone were structurally the simplest and hence the first to be added to cholesterol and the bile acids as known structures. Determination of the structures of the adrenocortical steroids in the late 30's represents the final dividend from structure studies begun nearly 40 years earlier. During the war period, 1940–48, the most significant accomplishment was the synthesis of cortisone from desoxycholic acid by L. H. Sarett at Merck and Company (*1*).[2]

In 1948 steroid research got a real "shot in the arm" when a practical utilization of an adrenocortical steriod was discovered. The dramatic anti-arthritic properties of cortisone, as reported by Hench, Kendall, Slocumb, and Polley (*2*) put steroids in the miracle drug class. From 1948 through 1953 research on synthesis of cortisone from alternate starting materials, including total synthesis, was the principal occupation of steroid chemists. Hydrocortisone was also synthesized during this period, and the isolation of aldosterone, the last biologically important adrenocorticoid, was reported.

The year 1953 begins the current phase of steroid research, that of chemical modification of the natural steroid hormones. It was in this year that Fried (*3*) found that a halogen atom could be inserted into the hydrocortisone molecule without obliteration, indeed with resultant enhancement, of biological activity. As a result 9α-fluorohydrocortisone was proven to be a useful topical agent for inflammatory conditions of the skin.

In 1955 the first systemically useful modified adrenocortical steroid was synthesized. This was done by insertion of a double bond into the 1,2-position of either cortisone or hydrocortisone (*4*). The resultant compounds, called prednisone and prednisolone, have been widely used in a variety of disease conditions. In additon to being more active than the natural hormones, they also exhibited less water and salt retention than cortisone or hydrocortisone.

This brief historical sketch brings us to the point of the beginning of this review. We will be considering in greater detail advances in steroid research in the period since 1955.

It is of interest to examine the publication of papers in the steroid field in the light of the historical background which has been cited.[3] The total number of steroid papers published through 1958 is about 4300. Of the 4300 papers published, roughly one quarter can be found in the literature prior to 1940. Approximately another quarter of the papers are in the literature from 1940 through 1950. Roughly one half of all steroid papers have been published *since 1950*. For the past six years, which follow Fried's report of the first useful modified adrenocortical steroid, papers have been produced at a rate of about 250 per year.

This tremendous increase in research can be accounted for in terms of an economic stimulus. Sales of steroid hormones during the past 10 years have increased at a truly remarkable rate. The anti-inflammatory steroids, encompassing modifications of adrenocortical steroids as well as the natural hormones themselves, last year in this country alone accounted for total sales of more than $100 million. This figure is only surpassed by antibiotics, vitamins, proprietary and other ethical pharmaceuticals, and tranquillizers. The sex hormones, and modifications thereof, represent another $25 million in sales to the pharmaceutical industry.

Steroid research today is highly competitive. Chemical structure-biological activity relationships have been

Presented at the 21st NEACT Summer Conference, University of Connecticut, Storrs, August 21, 1959.

[1] Presented while the author was associated with Merck Sharp and Dohme Research Laboratories, Rahway, New Jersey.

[2] Dr. Sarett has recently presented an excellent review of the past fifty years of research in the field of hormones including the steroids: THIS JOURNAL, **37**, 184 (1960).

[3] The author is indebted to Professor L. F. Fieser of Harvard University for data on published steroid papers.

developed to the stage where there has been some duplication of effort in synthesizing new modifications of the steroids. This is because any discovery of a new structural modification can make a sizable change almost overnight in the steroid profit distribution of the pharmaceutical companies involved. The public is the ultimate beneficiary from these research efforts as more steroids are becoming available for broadened medical usage.

Medical Uses

What are the medical uses to which these various classes of steroids can be put?

The anti-inflammatory steroids are used in the treatment of rheumatoid arthritis, skin allergies, eye inflammations, asthma, and general allergic abnormalities. These uses are perhaps best known so will not be discussed in any greater detail.

Progestational agents, or progestogens, can be used to *preserve, promote, or prevent pregnancy.* The preservation of pregnancy is a well-known function of progesterone, the natural hormone. The promotion and the prevention of pregnancy are more recent findings. This divergence of functions seems at first irreconcilable. However, the use of a progestogen to either prevent or to promote pregnancy is only understandable in terms of how the agent is used. For example, the promotion of pregnancy can be accomplished in the treatment of women who have abnormalities in the luteal phase of the menstrual cycle. A progestogen is administered beginning a day or two *after ovulation has occurred.* The agent is administered daily for about 10 days and then on alternate days until menstruation or pregnancy has been determined to occur. In this way, many women who had been unable to conceive because the fertilized ovum did not become attached to the uterine wall have become pregnant.

In contrast to this method of administration, the prevention of pregnancy is accomplished in the following way: the progestogen is administered beginning with day 5 after menstruation and continued through day 20. In this way *ovulation is inhibited.* If no ovum is released, pregnancy cannot occur. The ovulation inhibition or anovulatory effect is probably mediated through inhibition of gonadotrophin secretion by the pituitary gland. It is important to emphasize here that not all progestogens act as anovulatory agents. This point will be enlarged upon later.

The male sex hormones, or androgens, are largely used for their anabolic properties, i.e., their ability to cause retention of nitrogen. Anabolic effects are important in a variety of geriatric problems in which protein storage is critical: for example, in the treatment of various carcinomas, in the treatment, more specifically, of mammary cancer, and in post-operative recovery periods in a hospital. For these uses the androgenic properties of these steroids must be diminished while maintaining the anabolic properties. This, of course, is necessary if one is to use the agents for treatment of female as well as male patients. Partial success in the separation of anabolic and androgenic properties has been achieved in some of the newer agents, and clinical studies of these have been expanded during the past several years.

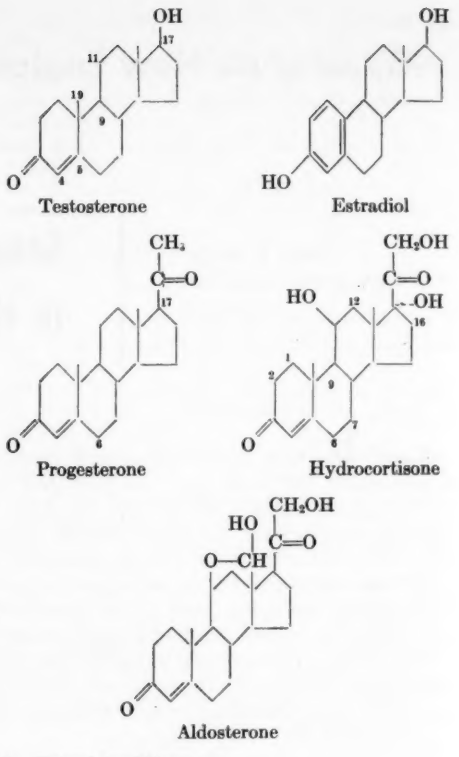

Figure 1. Natural steroid hormones.

The female sex hormones, or estrogens, are used for the treatment of various menstrual disorders. The largest current use for estrogens, however, is in the veterinary field. It has been found that estrogens, and particularly the synthetic estrogen stilbestrol, cause increased rate of fattening in cattle.

Aldosterone antagonists are useful for the treatment of patients who retain too much salt and water. That is, they are diuretic steroids. Aldosterone is the natural hormone secreted by the adrenal gland which causes retention of salt and water by the kidney. In some cases of edema, which is due to water retention, antagonists for natural aldosterone have been helpful. These agents are used in conditions such as toxemia of pregnancy or generalized edema associated with cardiac difficulties.

Natural Hormones

In Figure 1 the structural formulas for the five naturally occurring steroid hormones, which are synthesized in our bodies every day, are depicted. All of them have three six-membered rings and one five-membered ring fused together in a characteristic fashion. Except for estradiol they all have two bridgehead methyl groups, represented by the short vertical line between the first and second and the third and fourth rings; they are almost completely saturated compounds. Oxygen, in the form of hydroxyl and keto groups, is the only other element present. In general, the molecules are flat with functional groups projecting above and below the general plane of the rings. Groups projecting above the plane of the rings are beta substituents and are indicated by solid lines; groups pro-

jecting below the plane are alpha and are represented by dotted lines. The numbering system of these compounds is not outlined in detail. However, a number of selected positions have had numbers placed next to them for use in the following discussion.

Anti-inflammatory Steroids

Two important structural modifications of the hydrocortisone molecule have been mentioned: 9α-fluorohydrocortisone and prednisolone. Replacement of a hydrogen at the nine position gives the former compound while introduction of a double bond between the one and two positions of hydrocortisone gives the latter compound. If both of these activity-enhancing groups are combined one obtains the compound 9α-fluoroprednisolone (*5*). Its biological activity is approximately 25 to 30 times that of hydrocortisone. However, it is a salt retainer in the same way that 9α-fluorohydrocortisone is. Halogen atoms, particularly chlorine and fluorine, have been introduced into the following positions of the hydrocortisone molecule: positions 2, 4, 6, 9, and 12. Biological activity has been most interesting in the case of the 6 and 9 substituted halocortocoids. An additional double bond in the 6–7 position has also been investigated; no marketable product has come from this work.

Adding a hydroxyl group to the hydrocortisone molecule in general diminishes activity. However, one compound in this category has achieved remarkable success as an anti-inflammatory agent. The compound is called triamcinolone and it is 16α-hydroxy-Δ^1-9α-fluorohydrocortisone (*6*). That is, it has an additional double bond in the 1-2 position, a fluorine atom at 9, and a hydroxyl group at 16. It is about 4 to 5 times hydrocortisone in potency and thus has activity comparable with prednisolone.

Probably the most useful activity enhancing group is the methyl group. When a methyl group was introduced into the 6α-position of prednisolone (*7*), another compound was produced which has achieved a fair share of the anti-inflammatory steroid market. Most recently the introduction of a methyl group into the 16α-position has given a very useful compound. 16α-methyl-9α-fluoroprednisolone or dexamethasone has no less than 25 to 30 times the potency of hydrocortisone (*8*). The 16α-methyl group has served to completely remove the salt retaining properties of the parent 9α-fluoroprednisolone.

At the present time then, there are five principal anti-inflammatory steroids on the market: hydrocortisone, prednisolone, triamcinolone, 6α-methylprednisolone, and dexamethasone. In addition may be included the 11-keto analogues of two of these, namely cortisone and prednisone. Thus at the present time the physician has a number of anti-inflammatory steroid agents at hand rather than cortisone which was the only agent available ten years ago. Because of individual patient differences and because of the variety of disease conditions in which these agents are effective, all of them occupy a place of importance in current medical practice.

Enhancement of biological activity of adrenocortical steroids has ceased to be the main motive for this type of steroid research. It is certain that steroid chemists will be more concerned in the future with modification of biological activities rather than just activity enhancement. Thus, elimination of some of the undesirable metabolic effects of the anti-inflammatory steroids would seem to be an important goal for the next decade of research in anti-inflammatory steroids.

Progestogens

There are two major classes of progestogens or progestational steroids. One of these is composed of compounds in which the progesterone molecule (Fig. 1) has been modified. The second class of compounds contains a 17α-ethynylcarbinol grouping (Fig. 2). The parent compound in this class is called ethisterone. It is more potent orally than progesterone even though its structure is quite different from the natural hormone. In general, the ethynylcarbinol class has potent oral activity whereas the progesterone class is most potent when injected. The ethynylcarbinol grouping is produced by reaction of a 17-ketone with acetylene in the presence of a basic catalyst.

Let us first consider the class of compounds which are modified progesterones. Most of the compounds with enhanced biological activity are composed of added substituent groups at either positions 6 or 17 or both. 6α-methyl, 6α-fluoro, and 6α-nitro progesterone all show enhanced progestational activity. The corresponding 6β-compounds are less active. Substituted 17α-progesterones in general also show enhanced activity: i.e., 17α-methyl, 17α-bromo, and 17α-acetoxy progesterone. The latter compound is the most interesting in this group. 17α-hydroxyprogesterone has practically no progestational activity and yet when it is acylated one obtains a very active compound. This is unusual since one might expect the body to be able to readily remove ester groups.

When the above activity enhancing groups were combined, even more potent progestational agents were obtained. More significantly, oral activity is conferred on these compounds. Thus, 6α-methyl-17α-acetoxyprogesterone (*9*) was the most potent oral progestogen known until several months ago. It has now been surpassed by the 6-halogen-Δ^6-17α-acetoxyprogester-

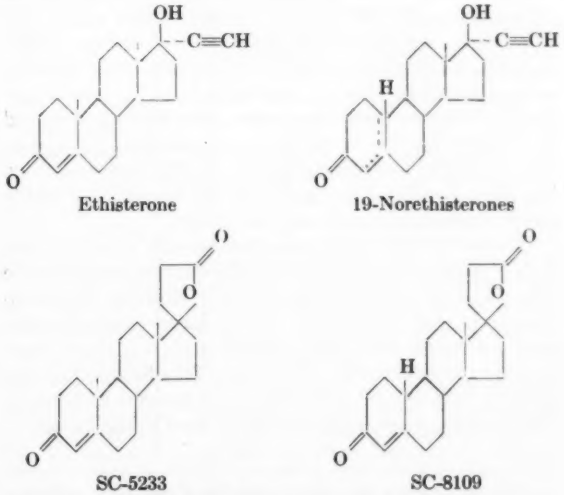

Figure 2. Progestogens and aldosterone antagonists.

ones (*10*). The most active compound in this series, 6-chloro-Δ^6-17α-acetoxyprogesterone is about 50 times as potent as Norlutin®, discussed below. This compound and its close relatives are currently undergoing extensive clinical trials.

Let us now turn to the 17α-ethynylcarbinol class of progestational agents. Norlutin® or 19-norethisterone (Fig. 2) is Parke Davis' orally active progestational agent. It has had the methyl group removed from the angular position between the first two rings of ethisterone. A double bond isomer of 19-norethisterone, in which the 4,5 double bond is shifted to the 5,10 position is called Enovid®. It is produced by G. D. Searle and Co. Both of these compounds are at present the most effective ovulation inhibiting agents in the field, although neither of them is recommended for this purpose at the present time.[4] Instead they are being marketed for treatment in threatened abortion and menstrual disorders while clinical evaluation of the anovulatory properties continues. Both compounds are highly active when administered by mouth.

6α,21-Dimethylethisterone (*11*), containing two additional methyl groups, showed quite markedly enhanced activity in animals. However, when this compound was tested clinically it apparently did not measure up to the animal data, and at present is not considered to be a leading candidate for progestogen usage.

The progestogen class is perhaps the most rapidly moving field of steroids at the present time. Interest in an effective, inexpensive agent for birth control has stimulated a concentrated effort by pharmaceutical companies in this area. Whether the expenditures of time and money will be justified remains to be seen. However, it seems probable that in the next few years an orally active ovulation inhibitor will appear on the market. The big question seems to be whether it will be priced low enough so that the people in this world who need it most can afford to buy it.

Androgen—Anabolic Steroids

At the present time there are three compounds being marketed in this field. Nilevar®, or 17α-ethyl-19-nortestosterone, is being produced by G. D. Searle and Company. It was the first compound subjected to clinical tests and the first one on the market in the field of anabolic agents (if one excludes testosterone esters and 17α-methyltestosterone which have been used for a long period of time). Halotestin®, or 9α-fluoro-11β-hydroxy-17α-methyltestosterone, has been introduced by Upjohn for use as an orally active androgen and to some extent as an anabolic agent. 4-Chlorotestosterone has been produced in Italy and has found a favorable reception among physicians in Europe.

In addition to these three compounds, several other very active derivatives of 4,5-dihydrotestosterone have been reported. Both Syntex and Sterling-Winthrop have reported compounds which have favorable animal activity. However, clinical data on these compounds are not available as yet. This field is just beginning to develop; it is difficult at present to forecast how broadly these reagents will be used in the future.

[4] Since this paper was written, the Food and Drug Administration has approved the use of Enovid® as an ovulation inhibitor.

Estrogens

Since most of the interest in this area has been concerned with animal fattening and involves the nonsteroidal synthetic estrogens, this topic will not be considered in detail. One comment, however, seems pertinent. Government control on the use of these potent compounds in animals which are to be consumed by humans will certainly have an influence on the future research in this area. Stilbestrol has been shown to be carcinogenic on prolonged administration to animals. Thus before new products are introduced to the animal feed industry, retention of the hormone in animal tissue must be determined.

Aldosterone Antagonists

The discovery that 17-spirolactones (Fig. 2) can antagonize the salt and water retention properties of natural aldosterone was of major importance. It was accomplished by chemists at Searle and they are the only ones to report findings in this field to date. The compounds have such a long chemical name and are so new that they are still designated by number and letter combination. SC-8109, the 19-nor analogue of SC-5233, is the more potent of the two compounds and also has good oral activity. Since removal of the 19-methyl group is an expensive process, a search for 19-methylspirolactones with activity comparable to SC-8109 was launched at Searle. The 7-thioacetate derivative of SC-5233 seems to have fulfilled this requirement (*12*). Further reports on its evaluation in the clinic will be forthcoming.

Summary

The past four years of research in the steroid field have been extremely fruitful. As a result our medical men have a number of good anti-inflammatory steroids to select from in prescribing for their patients. New highly potent progestogens are being synthesized almost too rapidly to be evaluated. Anabolic steroids are being produced at a more moderate rate, but there is the promise of better agents in this field as well. The aldosterone antagonist class of steroid has achieved the stage of development in which lowered costs may very soon allow marketing of a product. All of these facts promise greater things to come in this complex, rapidly moving field of chemical-biological research.

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Chem Ed

BOOK REVIEWS

Principles of Chemistry

Lejaren A. Hiller, Jr., University of Illinois, Urbana, and *Rolfe H. Herber*, Rutgers University, New Brunswick, New Jersey. McGraw-Hill Book Co., Inc., New York, 1960. xv + 735 pp. Figs. and tables. 15.5 × 23.5 cm. $7.75.

This is the text that teachers of general chemistry for students in the physical sciences, engineering and related fields or in "honor" sections will find most useful. It is written for the intelligent student who has had a good background in high school chemistry and who is prepared for college mathematics. The book is exceptionally well written, and even if it should not be suitable for a particular class the teacher will want it in his library for his own enjoyment.

The description of matter is treated in Part I and "The Dynamics of Chemical Change" in Part II. Fundamental concepts such as atomic structure, including quantum mechanical contributions, are reviewed in the first chapter. The covalent bond is discussed with emphasis on atomic orbital theory. One wonders why more is not said about other theories. Organic chemistry and inorganic compounds and their reactions are treated well in separate chapters. Inorganic coordination complexes are included in the chapter on the ionic bond.

Authentic physical chemistry is used throughout the text, hence treatment of such topics as the solid state, kinetic theory of gases, liquids and changes of state and the properties of metals is rigorous and meaningful. The nature of the metallic bond and Gibbs phase rule are just two items included which are not usually found in freshman texts.

The second part of the text deals mainly with physical chemistry. Equilibria, chemical thermodynamics, oxidation-reduction reactions, kinetics and catalysis, are the general areas covered. Such concepts as thermodynamic probability, entropy and free energy are introduced. The laws of thermodynamics, bond energies, reaction rates and orders, collision theory, and photochemistry are some of the topics included. There is a final chapter on radiochemistry and the nuclear properties of matter.

Each chapter is relatively self-contained to allow some flexibility in the selection and arrangement of material for specific courses. There is certainly enough material for a two-semester course. The authors suggest that it is also suitable for a "rigorous, rapidly paced one-semester course," but this would be true for only the exceptional classes.

Excellent questions and problems, some with answers given, follow each chapter. There are also some illustrative examples in the text itself. An instructor's manual with answers to all the problems is available to teachers. A review of mathematical operations is given in an appendix of the text. Also included is a bibliography of collateral reading selected from authoritative texts and articles from periodicals. These titles are grouped by chapters to follow the organization of the book.

Every teacher of general chemistry—indeed, every teacher of chemistry—will want to read this unique text. The authors are to be congratulated for their significant contribution.

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Successful Devices in Teaching Chemistry

Paul Westmeyer, University of Illinois Laboratory School. J. Weston Walch, Publisher, Portland, Maine, 1959. ii + 258 pp. Figs. 21.5 × 27.5 cm. Paperbound. $3.

The title is, perhaps, the most descriptive that could be chosen. The book opens with a statement of the author's philosophy with respect to a high school course in chemistry. It continues with a suggested core of fundamental content, urges extensive laboratory experience for students, makes suggestions for areas of special study, and concludes with a collection of interest catchers and student projects. Many of these were suggested and submitted by other teachers.

The introduction to the philosophy behind the course is most neatly given in a quotation from the yearbook of the National Society for the Study of Education, "Since the facts, concepts, and principles which we have emphasized in our teaching are really only the raw materials needed for carrying on the intellectual processes which govern behavior, we should recognize the incompleteness of teaching methods which place almost exclusive emphasis upon memorization and recall." The author quite appropriately concludes that effective learning takes place only when the student is interested and that student interest may and should be developed and guided by the teacher in the classroom. This is followed by a brief discussion of the learning theory which underlies the proposed method.

A fundamental core of material is given which includes the following concepts: atomic structure, bonding and valence, symbolism and equations, oxidation reduction, solutions and related phenomena, ionization and electrical phenomena, equilibrium and rates of reaction, gas behavior, periodic law, catalysis, neutralization and reactions among acids, bases and salts. The order of treatment of these topics is left to the discretion of the teacher.

It is proposed that the class work be developed in three stages. First will be a phase of study in which students are taught directively the basic concepts listed above in the core of fundamentals, including appropriate laboratory experiences to assist in the development of these

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Paul Westmeyer, Successful Devices in Teaching Chemistry

Paul Pascal, Nouveau Traite de Chimie Minerale. Volume 16

W. G. Palmer, Valency: Classical and Modern

Herbert S. Goldberg, Editor, Antibiotics: Their Chemistry and Non-Medical Uses

G. Malcolm Dyson in consultation with *Percy May*, May's Chemistry of Synthetic Drugs

Grafton D. Chase, Principles of Radioisotope Methodology

D. N. Underwood, Chemistry for Colleges and Schools

J. O. Hinze, Turbulence: An Introduction to Its Mechanism and Theory

Ibert Mellan and *Eleanor Mellan*, Removing Spots and Stains

C. H. Mathewson, Editor, Zinc: The Science and Technology of the Metal, Its Alloys and Compounds

I. L. Finar, Organic Chemistry. Volume 2: Stereochemistry and the Chemistry of Natural Products

Herbert W. Cremer and *Sidney B. Watkins*, Editors. Chemical Engineering Practice. Volume 11: Works Design, Etc.

concepts. Second will come a phase of small group study during which students in groups of three or four solve specific problems which have arisen as part of the course. This phase includes class work, library work, and laboratory work with appropriate emphasis on the laboratory work where students at first-hand discover, define, investigate, invent hypotheses, and devise experiments to test these hypotheses. At the conclusion of this phase, the students are expected to enter upon the third phase, individual study, wherein they identify, define and pursue problems which have arisen in previous work.

Following the work included in the fundamental core, a series of experiments involving qualitative analysis are recommended as a means of requiring individual planning and effort. At the conclusion of the work in qualitative analysis, students are expected to move on to an investigation of other problems of their choice. It is apparent to these reviewers that the suggestions made by the author can, and when effectively carried out will, lead to a very stimulating and successful high school course in chemistry. But it is equally apparent that this procedure can be carried out only by a teacher of considerable competence and considerable experience.

Part 2 consists of selections from fundamental content and is made up primarily of demonstrations and experiments which have been submitted by a variety of authors. Unfortunately, these have not been carefully edited and contain many booby traps for the unwary, including such statements as, on page 123, "sodium chloride *dissociates in water* to form sodium ions and chloride ions. These two ions with the ions of water can form sodium hydroxide and hydrochloric acid." While the conclusions are essentially correct, the implied mechanism is not.

Part 3 is devoted to safe and effective use of the laboratory. Again many useful techniques and devices are included which have been submitted by contributors. These reviewers must emphasize their reservations concerning the use of the laboratory without adequate responsible supervision.

Part 4, entitled areas of special study, includes many useful suggestions for work with colloids and organic chemistry which might be used by students who work more rapidly or which on occasion may be substituted for part of the core material for better students. Again, many of the items included here have been submitted by contributors. A number of more spectacular experiments have been included in chapter 14 under the heading of Special Demonstrations and Science Show Materials.

Part 5 is concerned with student projects, both student-directed and teacher-directed, and includes a number of suggestions submitted by contributors.

Part 6, which concludes this volume, contains suggestions for those teachers who might find themselves in a situation where they have no chemistry laboratory.

The preface opens with the statement that "This book is intended as an aid to the chemistry teacher." This is certainly true for a teacher reasonably well versed in the elements of chemistry. These reviewers, however, cannot agree that it should serve "the science teacher who has not been trained in chemistry but must teach this course because there is no one else to do it." A high degree of skill and a firm grasp of the subject are required for success with an open ended program. Many of the procedures described in the book would be extremely hazardous for the uninitiated.

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Nouveau Traité de Chimie Minérale. Volume 16

Paul Pascal, Membre de l'Institut, Professeur Honoraire a la Sorbonne. Masson Et Cie, Editeur Libraires de L'Academie de Medecine, Paris, 1960. xxxix + 1195 pp. Figs, and tables. 17.5 × 26 cm. Broché (two volumes) 170NF. Cartonné toile (one volume) 185NF.

Elements of Group VII, as subdivided into the halogens (F, Cl, Br, I, and At) and the transition metals (Mn, Tc, and Re), are discussed in this volume of Pascal's new treatise. Pascal himself has written introductions to the two subgroups, in addition to all the material on bromine and iodine. L. Domange, A. Chrétien, and M. Haïssinsky are the respective authors of the sections on fluorine, chlorine, and astatine. The material on manganese was written by M. Geloso and J. Faucherre, and S. Tribalat is author of the sections on technetium and rhenium. Part of the bibliography on chlorine was assembled by Joseph Heubel.

Bibliographical references total 9576. With the exception of the astatine bibliography, literature searches do not seem to have been conducted beyond 1958, and one of Pascal's own searches did not go beyond January 1, 1956.

The volume examined by the reviewer did not appear to measure up to standards of binding observed in earlier volumes. The index is not as thorough as might be expected for a volume which includes the halogens, but while criticisms may be made, the work does measure up to the generally good standards of the treatise as a whole. The supplementary volume of Mellor on the halogens published in 1956, in addition to being in English, has other advantages over Pascal's treatise, but the time lag in publishing supplements for Gmelin, as well as its plan of coverage through 1949 only, gives obvious advantages to the Pascal volume. Despite some shortcomings, this volume with others of the set published previously will make the Pascal treatise not only a desirable but almost a necessary reference tool in inorganic chemistry.

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Valency: Classical and Modern

W. G. Palmer, Fellow of St. John's College, Cambridge University. 2nd ed. Cambridge University Press, New York, 1959. ix + 244 pp. 61 figs. and 43 tables. 15 × 22 cm. $5.50.

This book emphasizes the fact that valency is a chemical concept that was well developed before the development of the modern physical theories that are now considered to be basic to its understanding. The first three chapters briefly survey the historical background, the methods of determining structure, and the distribution of valencies in the periodic table. The last three chapters are an introduction to the modern views of valency and some special topics such as hydrogen bonding and electron deficient compounds. The fourth chapter, a very elementary discussion restricted to the elements before the first transition group, is said to provide, together with the first three chapters, "a compact but elementary account of classical and modern conceptions of valency, suitable for the general reader."

The style is good, the abundant factual material seems well documented, and the numerous tables and figures are well chosen and clearly presented. In particular there is always a clear distinction made in the diagrams between lines connecting atoms or ions and lines outlining geometrical figures.

There are some things, however, that detract from the over-all excellence. One, a result of the historical approach, is the use in the first part of the book of "bond diagrams" in which each bond line represents one valence unit, not a shared pair of electrons. This leads to formulations such as N≡N=O. The author has also added the term "co-ionic" to the long list of synonyms for the coordinate covalent bond. On page 95 the name "periodic acid" is called a misnomer because the compound does not contain a peroxy group. On page 58 the term carbide is said to be reserved for salts containing the $C_2^{=}$ ion, thus pushing compounds such as Fe_3C and Be_2C into a nameless limbo and drawing an unwarranted distinction between covalent and ionic acetylides.

A discussion of the meanings of the terms valence, valency, and oxidation number would have been a welcome addition.

Because of the very elementary level of treatment, this is not a suitable book for a text even in undergraduate courses. However it would make a very good outside reading assignment. A good high school student with a year of chemistry could read much of it with profit. Even graduate students would do well to familiarize themselves with the classical background of valence theory. Not least of all, teachers will find much interesting factual material and some new ways of presenting rather complicated material in an elementary fashion.

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(Continued on page A550)